

414 Rec'd PCT/PTO 2 6 JUN 2000

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Form PTO-1390 REV. 10-94)		U. S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE	ATTORNEYS DOCKET NUMBER <b>RN97162G1</b>
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/elected office (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371			U.S. APPLICATION NO. (IF KNOWN, SEE 3737 CFR 1.5) <b>09/582390</b> NOT APPLICABLE
INTERNATIONAL APPLICATION NO. <b>PCT/FR98/02867</b>	INTERNATIONAL FILING DATE <b>December 23, 1998</b>	PRIORITY DATE CLAIMED <b>December 31, 1997 and July 30, 1998</b>	
TITLE OF INVENTION <b>PROCESS FOR SYNTHESIZING BLOCK POLYMERS BY CONTROLLED RADICAL POLYMERIZATION FROM DITHIOCARBAMATE COMPOUNDS</b>			
APPLICANT (S) FOR DO/EO/US: <b>Pascale CORPART, Dominique CHARMOT, Samir ZARD, Xavier FRANCK, and Ghenwa BOUHADIR</b>			
Applicant herewith submits the United States Designated/Elected Office (DO/EO/US) the following items and other information:			
1 <input checked="" type="checkbox"/> This is a <b>FIRST</b> submission of items concerning a filing under 35 U S C 371 2 <input type="checkbox"/> This is a <b>SECOND</b> or <b>SUBSEQUENT</b> submission of items concerning a filing under 35 U S C 371 3 <input checked="" type="checkbox"/> This express request to begin national examination procedures (35 U S C 371) (f) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U S C 371 (b) and PCT Articles 22 and 39(1) 4 <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date 5 <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U S C 371(c)(2)) a. <input type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau). b. <input checked="" type="checkbox"/> has been transmitted by the International Bureau. c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US) 6 <input checked="" type="checkbox"/> A translation of the International Application into English (35 U S C 371(c)(2)). 7 <input checked="" type="checkbox"/> A copy of the International Search Report (PCT/ISA/210) 8 <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U S C 371(c)(2)). a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International b. <input type="checkbox"/> have been transmitted by the International Bureau c. <input type="checkbox"/> have not been made, however the time limit for making such amendments has NOT expired. d. <input checked="" type="checkbox"/> have not been made and will not be made. 9 <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U S C 371(c)(3)). 10 <input checked="" type="checkbox"/> A oath or declaration of the inventor(s) (35 U S C 371(c)(4)). ( <b>unsigned</b> ) 11 <input checked="" type="checkbox"/> A copy of the International Preliminary Examination Report (PCT/IPEA/409). 12 <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U S C 371(c)(5)). <b>Items 13 to 18 below concern document(s) or information included:</b> 13 <input type="checkbox"/> An information Disclosure Statement under 37 CFR 1.97 and 1.98 14 <input type="checkbox"/> An assignment document for recording A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included 15 <input checked="" type="checkbox"/> A <b>FIRST</b> preliminary amendment A <b>SECOND</b> or <b>SUBSEQUENT</b> preliminary amendment 16 <input type="checkbox"/> A substitute specification. 17 <input type="checkbox"/> A change of power of attorney and/or address letter 18 <input checked="" type="checkbox"/> Certificate of Mailing by Express Mail 19 <input checked="" type="checkbox"/> Other items or information <b>Forms PCT/IB/308 and 332, PCT/ISA/210, PCT/IPEA/416 and 409 PCT/FR98/02867 as published</b>			

US APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.5) <div style="font-size: 2em; font-weight: bold; margin-top: 10px;">09/582390</div>	INTERNATIONAL APPLICATION NO. <b>PCT/FR98/02867</b>	ATTORNEY DOCKET NUMBER <b>RN97162G1</b>						
20 <input checked="" type="checkbox"/> The following fees are submitted: <b>BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):</b> Search Report has been prepared by the EPO or JPO..... <b>\$930.00</b>  International preliminary examination fee paid to USPTO (37 CFR 1,482) ..... <b>\$720.00</b> No international preliminary examination fee paid to USPTO (37 CFR 1,482) but international search fee paid to USPTO (37 CFR 1,4445 (a)(2))... <b>\$790.00</b>  Neither International preliminary examination fee (37 CFR 1,482) nor international search fee (37 CFR 1,4445 (a)(2)) paid to USPTO.. <b>\$970.00</b>  International preliminary examination fee paid to USPTO (37 CFR 1,482) and all claims satisfied provisions of PCT Article 33(2)-(4) ..... <b>\$ 98.00</b>  <div style="text-align: center;"><b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b></div>		<b>CALCULATIONS PTO USE ONLY</b>          <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 10%; text-align: right;">\$</td> <td style="width: 40%;">840.00</td> <td style="width: 50%;"></td> </tr> <tr> <td style="text-align: right;">\$</td> <td>0.00</td> <td></td> </tr> </table>	\$	840.00		\$	0.00	
\$	840.00							
\$	0.00							
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1,492(e)).								
<b>CLAIMS</b>	<b>NUMBER FILED</b>	<b>NUMBER EXTRA</b>						
Total Claims	24-20=	4						
Independent Claims	1-3=	0						
MULTIPLE DEPENDENT CLAIMS(S) (if applicable) 0		+\$260.00						
<b>TOTAL OF ABOVE CALCULATIONS =</b>		<b>\$ 912.00</b>						
Reduction by 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28)								
<b>SUBTOTAL =</b>		<b>\$ 912.00</b>						
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1,492 (f)).		\$ 0.00						
<b>TOTAL NATIONAL FEE =</b>		<b>\$ 912.00</b>						
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +		\$ 0.00						
<b>TOTAL FEES ENCLOSED =</b>		<b>\$ 912.00</b>						
		Amount to be refunded \$						
		charged \$						
a <input type="checkbox"/> A check in the amount of \$ _____ to cover the above fees is enclosed  b <input checked="" type="checkbox"/> Please charge my Deposit Account No. <b>18-1171</b> in the amount of <b>\$912.00</b> to cover the above fees.  c <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <b>18-1171</b> A duplicate copy of this sheet is enclosed.  <b>NOTE: Where an appropriate time limit under 37 CFR 1,494 or 1,495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.</b>								
SEND ALL CORRESPONDENCE TO: <b>Jean-Louis SEUGNET</b> <b>RHODIA INC.</b> <b>259 Prospect Plains Road</b> <b>CN 7500</b> <b>Cranbury, NJ 08512</b>		<div style="text-align: center;">             SIGNATURE  <b>Jean-Louis SEUGNET</b>            NAME            Limited Recognition under 37 CFR § 10.9(b) enclosed.         </div>						
<b>June 26, 2000</b> DATE		REGISTRATION NUMBER						

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In the Application of: **Pascale CORPART, Dominique CHARMOT, Samir ZARD, Xavier FRANCK and Ghenwa BOUHADIR**

National Phase of PCT/FR98/02867

International Filing Date: December 23, 1998

Serial No.:

Filed: June 26, 2000

**For: PROCESS FOR SYNTHESIZING BLOCK POLYMERS BY  
CONTROLLED RADICAL POLYMERIZATION FROM  
DITHIOCARBAMATE COMPOUNDS**

Assistant Commissioner for Patents  
Washington, D.C. 20231

**PRELIMINARY AMENDMENT**

Dear Sir:

Prior to the calculation of the filing fees, please enter the following amendment in the specification and claims.

Please amend the application as follows:

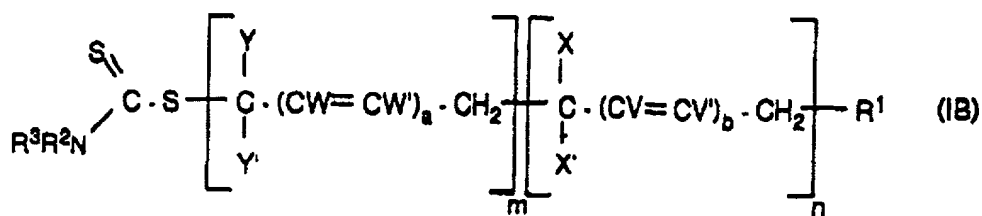
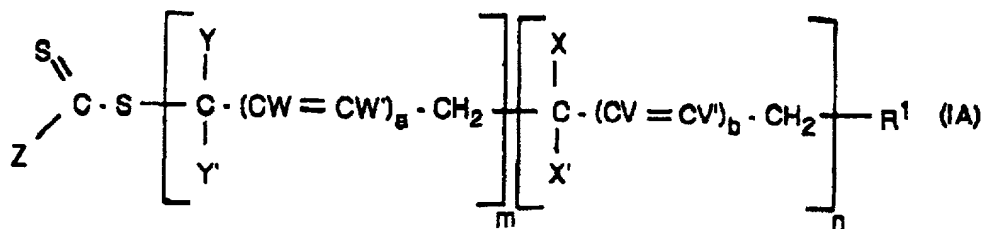
In the specification:

Page 1, just after the title, please add: - - This application is an application under 35 U.S.C. Section 371 of International Application Number PCT/FR98/02867 filed on December 23, 1998.- -

In the claims:

Please cancel claims 1 to 28 and add the following claims 29 to 52:

29. A process for preparing block polymers of general formula (IA) or (IB):



in which formulae:

-  $\text{R}^1$  represents:

an optionally substituted alkyl, acyl, aryl, alkene or alkyne group (i),  
an optionally substituted or aromatic, saturated or unsaturated, carbocycle (ii), or  
an optionally substituted or aromatic, saturated or unsaturated, heterocycle (iii),  
optionally, these groups and rings (i), (ii) and (iii) are substituted with substituted  
phenyl groups, substituted aromatic groups, or groups: alkoxycarbonyl or  
aryloxycarbonyl (-COOR), carboxyl (-COOH), acyloxy (-O<sub>2</sub>CR), carbamoyl  
(-CONR<sub>2</sub>), cyano (-CN), alkylcarbonyl, alkylarylcarbonyl, arylcarbonyl,  
arylalkylcarbonyl, phthalimido, maleimido, succinimido, amidino, guanidino,  
hydroxyl (-OH), amino (-NR<sub>2</sub>), halogen, allyl, epoxy, alkoxy (-OR), S-alkyl, S-aryl,

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**National Phase of PCT/FR98/02867**  
**PRELIMINARY AMENDMENT**

organosilyl, groups having a hydrophilic or ionic character, such as the alkali metal salts of carboxylic acids, the alkali metal salts of sulphonic acid, polyalkylene oxide chains (PEO, PPO), cationic substituents (quaternary ammonium salts),

R representing an alkyl or aryl group,

- Z is an optionally substituted ring comprising a nitrogen atom via which Z is linked to the C(=S)-S- group of formula (IA), the other atoms of said ring inducing a delocalizing or electron-withdrawing effect with respect to the electron density of the nitrogen atom,

-R<sup>2</sup> and R<sup>3</sup>, which are identical or different, represent:

an optionally substituted alkyl, acyl, aryl, alkene or alkyne group (i),

an optionally substituted or aromatic, saturated or unsaturated, carbocycle (ii), or

an optionally substituted, saturated or unsaturated, heterocycle (iii),

optionally, these groups and rings (i), (ii) and (iii) are substituted with:

. substituted phenyl groups or substituted aromatic groups,

. groups: alkoxycarbonyl or aryloxycarbonyl (-COOR), carboxyl (-COOH),

acyloxy (-O<sub>2</sub>CR), carbamoyl (-CONR<sub>2</sub>), cyano (-CN), alkylcarbonyl,

alkylarylcarbonyl, arylcarbonyl, arylalkylcarbonyl, phthalimido, maleimido,

succinimido, amidino, guanidino, hydroxyl (-OH), amino (-NR<sub>2</sub>), halogen,

allyl, epoxy, alkoxy (-OR), S-alkyl, S-aryl,

. groups having a hydrophilic or ionic character, such as the alkali metal salts of carboxylic acids, the alkali metal salts of sulphonic acid, polyalkylene oxide chains (PEO, PPO), cationic substituents (quaternary ammonium salts),

R representing an alkyl or aryl group,

and, for at least  $R^2$  or  $R^3$ , these groups and rings (i), (ii) and (iii) induce a delocalizing or electron-withdrawing effect with respect to the electron density of the nitrogen atom to which  $R^2$  and  $R^3$  are linked,

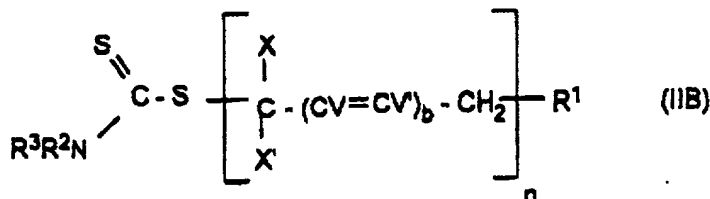
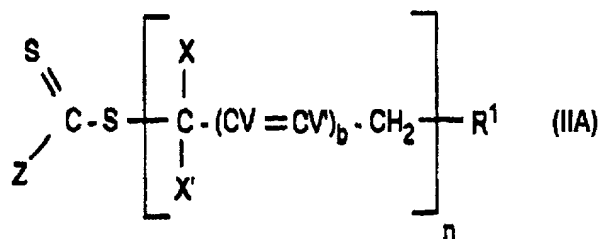
- V, V', W and W', which are identical or different, represent: H, an alkyl group or a halogen,
- X, X', Y and Y', which are identical or different, represent H, a halogen, a group  $R'$ ,  $OR'$ ,  $OCOR'$ ,  $NHCOH$ ,  $OH$ ,  $NH_2$ ,  $NHR'$ ,  $N(R')_2$ ,  $(R')_2N^+O^-$ ,  $NHCOR'$ ,  $CO_2H$ ,  $CO_2R'$ ,  $CN$ ,  $CONH_2$ ,  $CONHR'$  or  $CONR'_2$ , wherein  $R'$  is alkyl, aryl, aralkyl, alkaryl, alkene or organosilyl groups, optionally perfluorinated and optionally substituted with one or more carboxyl, epoxy, hydroxyl, alkoxy, amino, halogen or sulphonic groups,
- a and b, which are identical or different, are equal to 0 or 1,
- m and n, which are identical or different, are greater than or equal to 1 and, when one or other is greater than 1, the individual repeat units are identical or different,

said process comprising the step of bringing into contact with each other:

- an ethylenically unsaturated monomer of formula:



- a precursor compound of general formula (IIA) or (IIB):



wherein Z, X, X', V, V', R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> have the same meaning, and b and n the same value, as previously; and

- a radical polymerization initiator.

30. A process according to claim 29, wherein the ethylenically unsaturated monomer is styrene, butadiene, chloroprene, (meth)acrylic esters, or vinyl nitriles.

31. A process according to claim 29, wherein, in compounds of formula (IA) and (IIA), the ring Z is a ring made of carbon atoms.

32. A process according to claim 29, wherein the ring Z further comprises at least one heteroatom other than the nitrogen which links the ring Z to -C(=S)S, this heteroatom being O, S, N or P.

33. A process according to claim 29, wherein, in the compounds of formula (IA) and (IIA), the ring Z is an aromatic ring.

34. A process according to claim 29, wherein, in the compounds of formula (IA) and (IIA), the ring Z comprises at least one of the following functional groups:

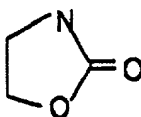
carbonyl (C=O), SO<sub>2</sub>, POR'', R'' representing an alkyl, aryl, OR, SR or NR<sub>2</sub> group, wherein the R group is identical or different and represents an alkyl or aryl group.

35. A process according to claim 29, wherein, in the compounds of formula (IA) and (IIA), the ring Z is substituted with at least one of the following groups: alkyl, aryl, alkoxycarbonyl or aryloxycarbonyl (-COOR), carboxyl (-COOH), acyloxy (-O<sub>2</sub>CR), carbamoyl (-CONR<sub>2</sub>), R representing an alkyl or aryl group, cyano (-CN), alkylcarbonyl, alkylarylcarbonyl, arylcarbonyl, arylalkylcarbonyl, phthalimido, maleimido, succinimido, amidino, guanidimo, hydroxyl (-OH), amino (-NR<sub>2</sub>), halogen, allyl, epoxy, alkoxy (-OR), S-alkyl, S-aryl, groups having a hydrophilic or ionic character, polyalkylene oxide chains, or cationic substituents.

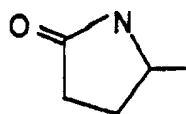
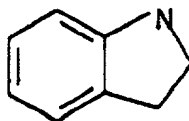
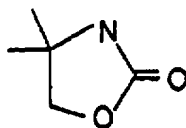
36. A process according to claim 29, wherein, in the compounds of formula (IA) and (IIA), the ring Z is substituted with at least one carbocycle or a heterocycle, optionally aromatic or substituted.

37. A process according to claim 36, wherein, in the compounds of formula (IA) and (IIA), the ring Z and its cyclic substituent have two common atoms.

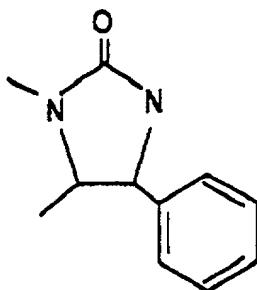
38. A process according to claim 29, wherein the ring Z is one of the following rings:







or

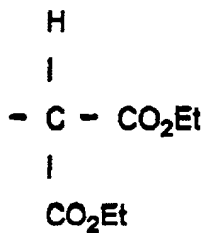
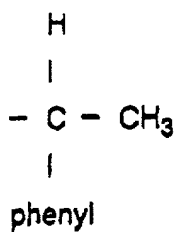
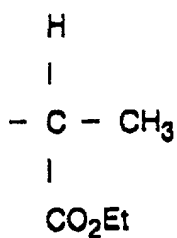


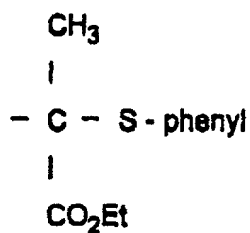
39. A process according to claim 29, wherein, in compounds of formula (IB) and (IIB),  $R^2$  or  $R^3$  exert a  $\pi$  withdrawing effect.
40. A process according to claim 40, wherein  $R^2$  or  $R^3$  represent a carbonyl or (hetero)aromatic group.

41. A process according to claim 40, wherein, in compounds of formula (IB) and (IIB),  $R^2$  or  $R^3$  exert a  $\Sigma$  withdrawing effect.

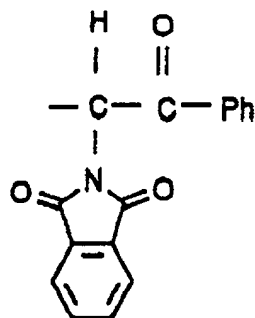
42. A process according to claim 29, wherein  $R^2$  or  $R^3$  represent an alkyl group substituted with electron-withdrawing groups.

43. A process according to claim 29, wherein  $R^1$  is one of the following groups:

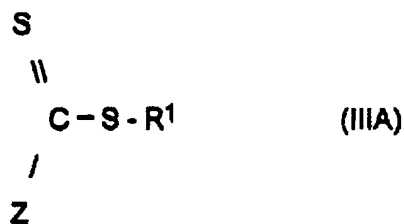


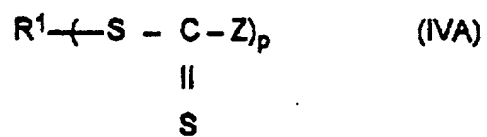


or



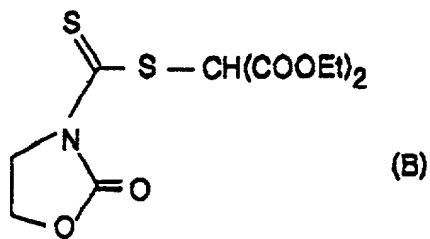
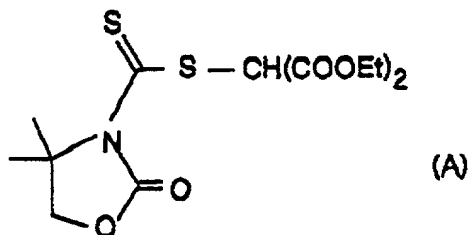
44. A process according to claim 29, wherein the precursor compound of general formula (IIA) is a polymer coming from the radical polymerization of an ethylenically unsaturated monomer of formula:  $\text{CXX}'(=\text{CV}-\text{CV}')_b=\text{CH}_2$  during which said monomer is brought into contact with a radical polymerization initiator and a compound of general formula (IIIA) or (IVA):





p being between 2 and 10.

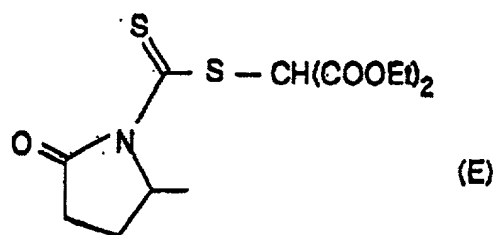
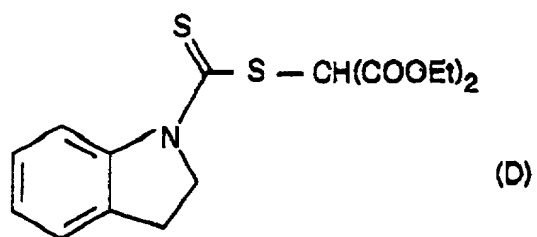
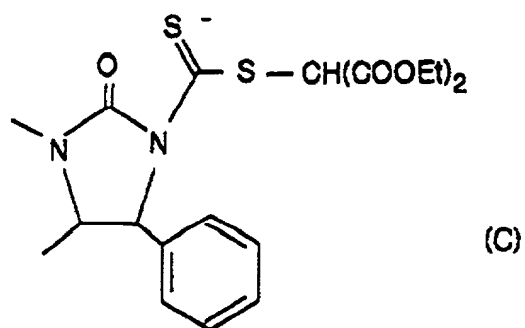
45. A process according to claim 44, wherein the compound of formula (IIIA) is a compound of the following formulae:

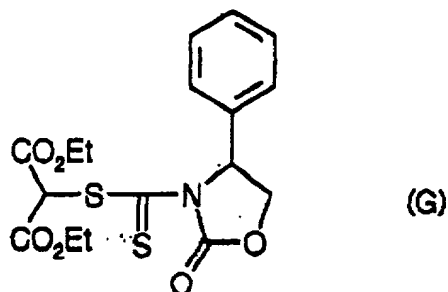
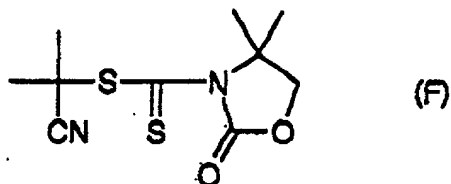


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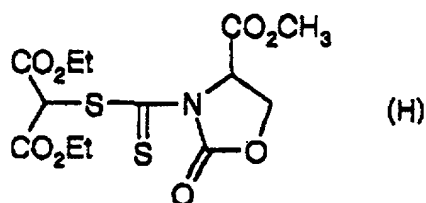
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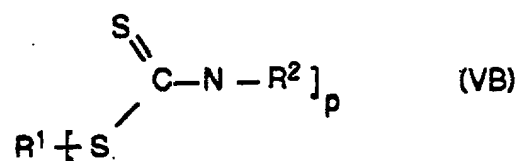
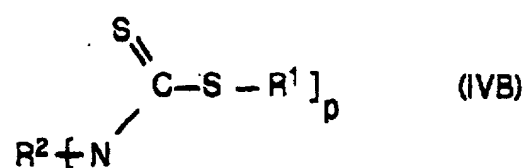
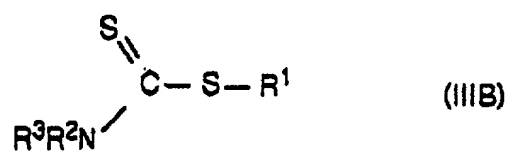




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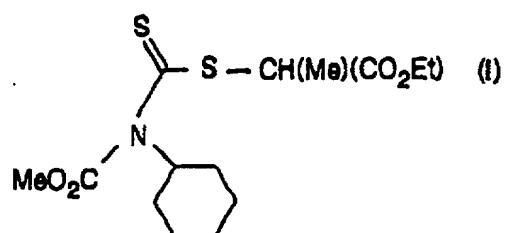


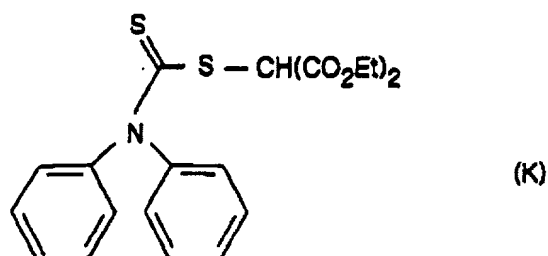
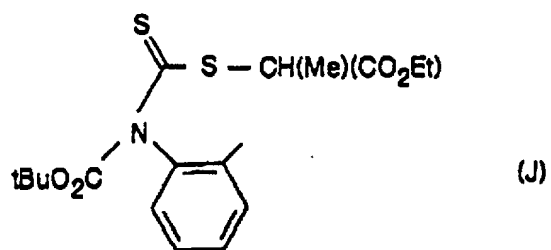
46. A process according to claim 29, wherein the precursor compound of general formula (IIB) is a polymer coming from the radical polymerization of an ethylenically unsaturated monomer of formula:  $CXX' (=CV-CV')_b=CH_2$  during which said monomer is brought into contact with a radical polymerization initiator and a compound of general formula (IIIB), (IVB) or (VB):



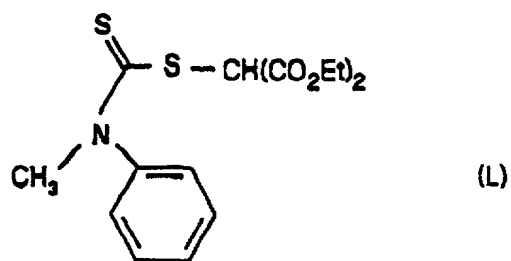
p being between 2 and 10.

47. A process according to claim 46, wherein the compound of formula (IIIB) is a compound of the following formulae:





or



48. A process for preparing multiblock polymers, comprising the step of:
- repeating at least once the implementation of the process of claim 29, using:
    - different monomers from those of the previous implementation, and



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- instead of the precursor compound of formula (IIA) or (IIB), the block polymer coming from the previous implementation.

49. Block polymer made by the process according to claim 29.
50. Block polymer according to claim 49, having a polydispersity index of at most 2.
51. Block polymer according to claim 50, having a polydispersity index of at most 1.5.
52. Block polymer according to claim 49, having at least two polymer blocks chosen from the following combinations:
  - polystyrene/polymethyl acrylate,
  - polystyrene/polyethyl acrylate,
  - polystyrene/poly(*tert*-butyl acrylate),
  - polyethyl acrylate/polyvinyl acetate,
  - polybutyl acrylate/polyvinyl acetate, or
  - poly(*tert*-butyl acrylate)/polyvinyl acetate.

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**REMARK:**

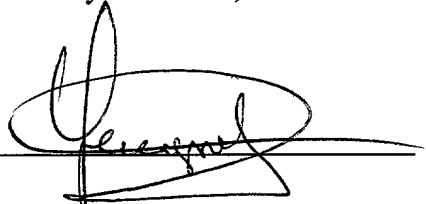
It is asserted that these amendments do not add new matter and are supported by the specification and claims as originally filed. Entry of these amendments is respectfully requested.

**June 26, 2000**

Rhodia Inc.  
259 Prospect Plains Road  
CN7500,  
Cranbury, NJ 08512

F/BREVET/RN97162G1.Prelim.Doc

Respectfully submitted,

By 

Jean-Louis SEUGNET  
Limited Recognition under 37 CFR §  
10.9(b) enclosed.  
Tel : (609) 860-4180  
Fax: (609) 860-0503

EL619399705US

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**PROCESS FOR SYNTHESIZING BLOCK POLYMERS  
BY CONTROLLED RADICAL POLYMERIZATION  
FROM DITHIOCARBAMATE COMPOUNDS**

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The present invention relates to a novel radical polymerization process for obtaining block copolymers.

Block polymers are usually prepared by ionic polymerization. This type of polymerization has several drawbacks:

- it only allows the polymerization of certain types of non-polar monomers, especially styrene and butadiene,
- it requires a particularly pure reaction mixture and temperatures which are often below room temperature so as to minimize parasitic reactions.

The operational constraints are therefore severe.

Radical polymerization has the advantage of being easily carried out without having to comply with excessive purity conditions, and at temperatures greater than or equal to room temperature. During this polymerization, macroradicals, which have a very short lifetime, recombine irreversibly by coupling or dismutation. When the polymerization takes place in the presence of several comonomers, the compositional variation of the mixture is infinitely low compared

with the lifetime of the macroradical so that the chains have a random sequence of monomer units and not a block-type sequence.

Consequently, until recently a radical  
5 polymerization process allowing block polymers to be obtained did not exist.

Since then, a new radical polymerization process has been developed, namely "controlled" or "living" radical polymerization. This controlled  
10 radical polymerization takes place by the growth, by propagation, of macroradicals.

At the present time, several controlled radical polymerization techniques are known, in which the ends of polymer chains may be reactivated in the  
15 form of a radical by homolytic bond (for example, C-O or C-halogen) scission.

Controlled radical polymerization therefore has the following distinct characteristics:

1. the number of chains is fixed throughout the  
20 duration of the reaction,
2. the chains all grow at the same rate, resulting in:
  - a linear increase in the molecular masses with conversion,
  - 25 • a narrow distribution of masses,
3. the average molecular mass is controlled by the monomer/chain-precursor molar ratio, and

4. the possibility of preparing block copolymers.

The controlled character is even more pronounced when the rate of consumption of the chain precursor is very much greater than the rate of growth of the chains (propagation). There are cases where this is not always true and conditions 1 and 2 are not observed, nevertheless it is always possible to prepare block copolymers.

Several approaches have been described for controlling radical polymerization. The most commonly cited consists in introducing, into the mixture, counter radicals which combine reversibly with the growing macroradicals, such as, for example, nitroxyl radicals (Georges et al., *Macromolecules*, **26**, 2987, (1993)). This technique is characterized by high temperatures for labilizing the C-O bond.

Another method, called Atom Transfer Radical Polymerization, makes use of transition metal salts combined with organic ligands and an initiator generally consisting of an organic halide; control of the polymerization is made possible by the reversible activation of the C-halogen bond (K. Matyjaszewski, *PCT WO 96/30421*). One drawback with this polymerization is that it requires a stoichiometric quantity of metal per chain precursor.

Otsu (Otsu et al., *Makromol. Chem. Rapid Comm.*, **3**, 127-132, (1982), Otsu et al. *ibid*, **3**, 123-140, (1982), Otsu et al., *Polymer Bull.*, **7**, 45, (1984),

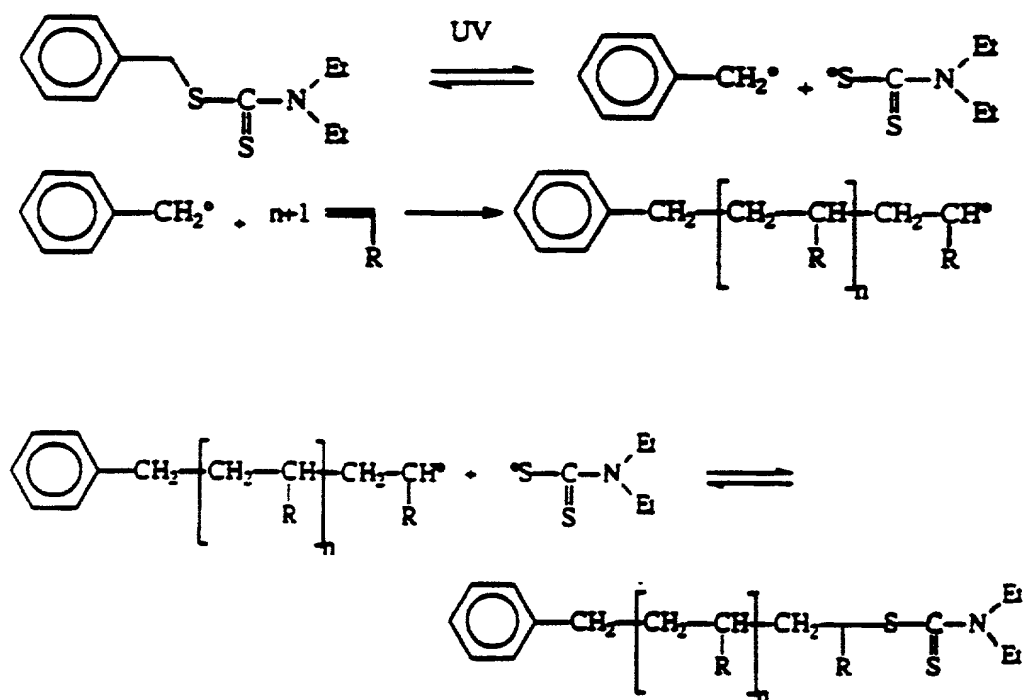
*ibid*, **11**, 135, (1984), Otsu et al, *J. Macromol. Sci.*

*Chem.*, **A21**, 961, (1984) and Otsu et al.,

*Macromolecules*, **19**, 2087, (1989)) has shown that

certain organic sulphides, particularly

- 5 dithiocarbamates, allowed chains to be grown in a controlled manner under UV irradiation, according to the principle:



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#### Reaction 1

The principle relies on the photolysis of the C-S bond, which regenerates the carbon macroradical, on the one hand, and the dithiocarbamyl radical, on the other hand. The controlled character of the reaction is due to the reversibility of the C-S bond under UV

irradiation. It is thus possible to obtain block copolymers. On the other hand, the rate of exchange in propagating species and "dormant" species of reaction 1 above is not very large compared with the rate of propagation, this having the consequence of generating relatively broad molecular mass distributions. Thus, the polydispersity index ( $PI = M_w/M_n$ ) is between 2 and 5 (Otsu et al., **25**, 7/8, 643-650, (1989)).

Xanthate disulphides and dithiocarbamate disulphides are themselves well known as transfer agents in conventional radical polymerization in thermal mode and in the presence of an initiator, but no one has hitherto been able to control the polymerization, or even less to produce block copolymers.

Up till now it was known that disulphides (tetraalkylthiuram disulphide, diisopropylxanthate disulphide and mercaptobenzothiazol disulphide) were activatable thermally or under UV irradiation, whereas monosulphides (substituted xanthates, dithiocarbamates) were activatable only under UV irradiation (Roha et al., *Macromol. Symp.*, **91**, 81-92, (1995), and Okawara et al., *Bull. of the Tokyo Inst. of Techn.*, No. 78, 1966).

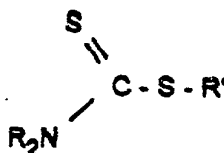
However, controlled radical polymerization making use of a UV irradiation source is very difficult to carry out, especially from an industrial standpoint, since the penetration of the UV photons into the polymerization medium is limited, both by absorption

phenomena (most of the ethylenic monomers absorb in the 210 - 280 nm range) and by diffusion phenomena in disperse media (suspension, emulsion).

Moreover, it has been shown (Turner et al.,  
5 *Macromolecules*, 23, 1856-1859, (1990)) that photopolymerization in the presence of dithiocarbamate generates carbon disulphide and may be accompanied by a loss of polymerization control.

For these reasons, it has thus been sought to  
10 develop a technique which can be used to obtain block copolymers by a process without UV irradiation, preferably by thermal initiation. Until the present time, no controlled radical polymerization system has been able to be demonstrated using dithiocarbamate  
15 compounds in the absence of a UV source.

Document WO 98/01478 describes a process for preparing block polymers by controlled radical polymerization. According to that document, such a process cannot be implemented with the aid of  
20 compounds, called chain-transfer agents, chosen from dithiocarbamates, of general formula:



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Controlled radical polymerization has an advantage over conventional radical polymerization when it is a question of preparing low-molecular-weight



functionalized chains (reactive telomers). Such polymers are desirable for specific applications such as, for example, coatings and adhesives.

Thus, when it is attempted to synthesize chains grafted with, on average, 2 functional comonomers, the fraction of chains with at most one functional site becomes large when the average degree of polymerization is less than a threshold value (e.g. 20 or 30). Controlled radical polymerization makes it possible to reduce, or even to inhibit, the formation of these oligomers having zero or one functional site which degrade the performance in terms of application.

One object of the present invention is to provide a novel controlled radical polymerization process for the synthesis of block polymers from dithiocarbamates.

Another object of the present invention is to provide a novel controlled radical polymerization process for the synthesis of block polymers from dithiocarbamates in the absence of a UV source.

Another object is to provide a controlled radical polymerization process for the synthesis of block polymers from all types of monomers.

Another object is to provide a controlled radical polymerization process for the synthesis of block polymers containing no metal impurities deleterious to their use.

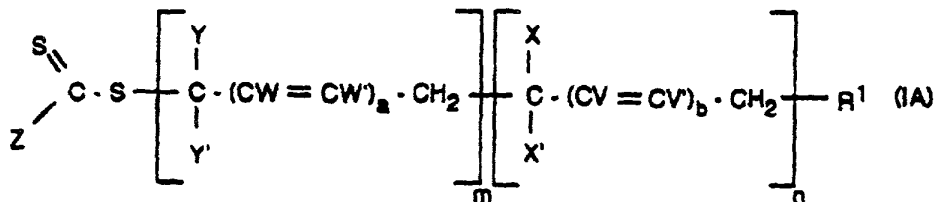
Another object is to provide a controlled

radical polymerization process for the synthesis of block copolymers, the said polymers being chain-end functionalized.

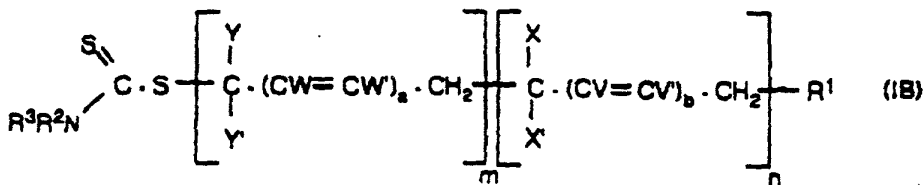
Another object is to provide a controlled radical polymerization process for the synthesis of block polymers and block copolymers having a low polydispersity index.

Another object is to provide a controlled radical polymerization process for the synthesis of oligomers in which the number of functional units is constant from chain to chain.

To these ends, the invention relates to a process for preparing block polymers of general formula (IA) or (IB):



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in which formulae:

-  $\text{R}^1$  represents:

- 20 • an optionally substituted alkyl, acyl, aryl, alkene or alkyne group (i), or

- an optionally substituted or aromatic, saturated or unsaturated, carbocycle (ii), or
  - an optionally substituted or aromatic, saturated or unsaturated, heterocycle (iii),
- 5 it being possible for these groups and rings (i), (ii) and (iii) to be substituted with substituted phenyl groups, substituted aromatic groups, or groups: alkoxycarbonyl or aryloxycarbonyl (-COOR), carboxyl (-COOH), acyloxy (-O<sub>2</sub>CR), carbamoyl (-CONR<sub>2</sub>),
- 10 cyano (-CN), alkylcarbonyl, alkylarylcarbonyl, arylcarbonyl, arylalkylcarbonyl, phthalimido, maleimido, succinimido, amidino, guanidimo, hydroxyl (-OH), amino (-NR<sub>2</sub>), halogen, allyl, epoxy, alkoxy (-OR), S-alkyl, S-aryl, organosilyl, groups having a
- 15 hydrophilic or ionic character, such as the alkali metal salts of carboxylic acids, the alkali metal salts of sulphonic acid, polyalkylene oxide chains (PEO, PPO), cationic substituents (quaternary ammonium salts),
- 20 R representing an alkyl or aryl group,
- Z is an optionally substituted ring comprising a nitrogen atom via which Z is linked to the C(=S)-S-group of formula (IA), the other atoms of the said ring inducing a delocalizing or electron-withdrawing effect
- 25 with respect to the electron density of the nitrogen atom,
- R<sup>2</sup> and R<sup>3</sup>, which are identical or different, represent:
- an optionally substituted alkyl, acyl, aryl,

- an optionally substituted or aromatic, saturated or unsaturated, carbocycle (ii), or
- an optionally substituted, saturated or unsaturated, heterocycle (iii),

5 it being possible for these groups and rings (i), (ii) and (iii) to be substituted with:

10 . groups: alkoxycarbonyl or aryloxy carbonyl  
(-COOR), carboxyl (-COOH), acyloxy (-O<sub>2</sub>CR),  
carbamoyl (-CONR<sub>2</sub>), cyano (-CN), alkylcarbon  
alkylarylcarbonyl, arylcarbonyl,  
arylalkylcarbonyl, phthalimido, maleimido,

. groups having a hydrophilic or ionic character, such as the alkali metal salts of carboxylic acids, the alkali metal salts of sulphonic acid, polyalkylene oxide chains (PEO, PPO), cationic substituents (quaternary ammonium salts),

and, for at least  $\mathbf{R}^2$  or  $\mathbf{R}^3$ , these groups and rings (i),

25 (ii) and (iii) induce a delocalizing or electron-withdrawing effect with respect to the electron density of the nitrogen atom to which  $R^2$  and  $R^3$  are linked,

-  $V, V', W$  and  $W'$ , which are identical or different,

represent: H, an alkyl group or a halogen,

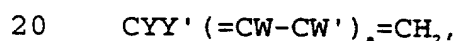
- **X**, **X'**, **Y** and **Y'**, which are identical or different, represent H, a halogen or a group chosen from  $R'$ ,  $OR'$ ,  $OCOR'$ ,  $NHCOH$ ,  $OH$ ,  $NH_2$ ,  $NHR'$ ,  $N(R')_2$ ,  $(R')_2N^+O^-$ ,  $NHCOR'$ ,  $CO_2H$ ,  $CO_2R'$ ,  $CN$ ,  $CONH_2$ ,  $CONHR'$  or  $CONR'_2$ , in which  $R'$  is chosen from alkyl, aryl, aralkyl, alkaryl, alkene or organosilyl groups, optionally perfluorinated and optionally substituted with one or more carboxyl, epoxy, hydroxyl, alkoxy, amino, halogen or sulphonic groups,

- **a** and **b**, which are identical or different, are equal to 0 or 1,

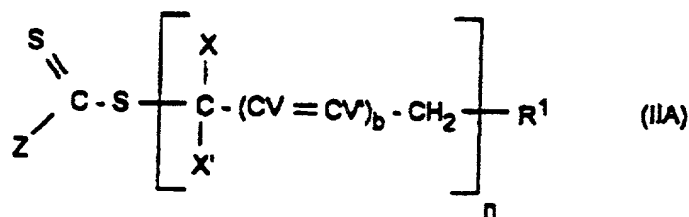
- **m** and **n**, which are identical or different, are greater than or equal to 1 and, when one or other is greater than 1, the individual repeat units are identical or different,

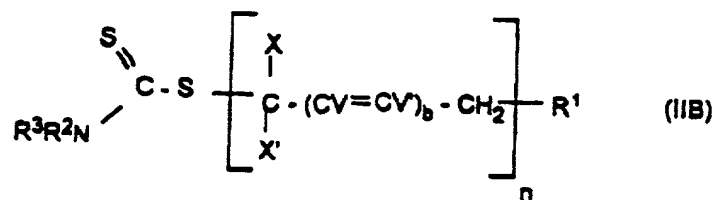
in which process the following are brought into contact with each other:

- an ethylenically unsaturated monomer of formula:



- a precursor compound of general formula (IIA) or (IIB):





in which Z, X, X', V, V', R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> have the same meaning, and b and n the same value, as previously,  
 - a radical polymerization initiator.

5           The process therefore consists in bringing into contact with each other a radical polymerization initiator, an ethylenically unsaturated monomer and a precursor of general formula (IIA) or (IIB).

**The radical polymerization initiator** may be  
 10 chosen from the initiators conventionally used in radical polymerization. These may, for example, be one of the following initiators:

- hydrogen peroxides such as: *tert*-butyl hydroperoxide, cumene hydroperoxide, *tert*-butyl peroxyacetate, *tert*-butyl peroxybenzoate, *tert*-butyl peroxyoctoate, *tert*-butyl peroxyneodecanoate, *tert*-butyl peroxyisobutyrate, lauroyl peroxide, *tert*-amyl peroxy-pivalate, *tert*-butyl peroxy-pivalate, dicumyl peroxide, benzoyl peroxide, potassium persulphate and
- 20 ammonium persulphate;
- azo compounds such as: 2-2'-azobis(isobutyronitrile), 2,2'-azobis(2-butanenitrile), 4,4'-azobis(4-pentanoic acid), 1,1'-azobis(cyclohexanecarbonitrile), 2-(*tert*-butylazo)-

2-cyanopropane, 2,2'-azobis[2-methyl-N-(1,1)-  
 bis(hydroxymethyl)-2-hydroxyethyl]propionamide, 2,2'-  
 azobis(2-methyl-N-hydroxyethyl]propionamide, 2,2'-  
 azobis(N,N'-dimethyleneisobutyramidine) dichloride,  
 5 2,2'-azobis(2-amidinopropane) dichloride, 2,2'-  
 azobis(N,N'-dimethyleneisobutyramide), 2,2'-  
 azobis(2-methyl-N-[1,1-bis(hydroxymethyl)-  
 2-hydroxyethyl]propionamide), 2,2'-azobis(2-methyl-  
 N-[1,1-bis(hydroxymethyl)ethyl]propionamide), 2,2'-  
 10 azobis[2-methyl-N-(2-hydroxyethyl)propionamide] and  
 2,2'-azobis(isobutyramide) dihydrate;

- redox systems including combinations such  
 as:

. mixtures of hydrogen peroxide or alkyl  
 15 peroxide, peresters, percarbonates and the like and of  
 any one of the salts of iron, titanous salts, zinc  
 formaldehyde sulfoxylate or sodium formaldehyde  
 sulfoxylate, and reducing sugars;

. alkali-metal or ammonium persulphates,  
 20 perborates or perchlorates in combination with an  
 alkali metal bisulphite, such as sodium metabisulphite,  
 and reducing sugars;

. alkali-metal persulphates in combination  
 with an arylphosphinic acid, such as benzenephosphonic  
 25 acid and other similar acids, and reducing sugars.

Preferably, the amount of initiator to be  
 used is determined so that the amount of radicals  
 generated is at most 25 mol% with respect to the amount

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of compound (IIA) or (IIB), even more preferably at most 15 mol%.

As **ethylenically unsaturated monomer**, the monomers chosen from styrene or its derivatives, butadiene, chloroprene, (meth)acrylic esters, vinyl esters and vinyl nitriles are more specifically used according to the invention.

Butadiene and chloroprene correspond to the case in which a and b = 1 in the formulae (IA), (IB), (IIA) or (IIB) and in the formula for the monomer given above.

"(Meth)acrylic esters" should be understood to mean esters of acrylic acid and of methacrylic acid with hydrogenated or fluorinated C<sub>1</sub>-C<sub>12</sub>, preferably C<sub>1</sub>-C<sub>8</sub>, alcohols. Among compounds of this type, mention may be made of: methyl acrylate, ethyl acrylate, propyl acrylate, n-butyl acrylate, isobutyl acrylate, 2-ethylhexyl acrylate, tert-butyl acrylate, methyl methacrylate, ethyl methacrylate, n-butyl methacrylate and isobutyl methacrylate.

The vinyl nitriles include more particularly those having from 3 to 12 carbon atoms, such as, in particular, acrylonitrile and methacrylonitrile.

It should be noted that styrene may be replaced, completely or partly, by derivatives such as alpha-methylstyrene or vinyltoluene.

The other ethylenically unsaturated monomers which can be used, alone or as mixtures, or which can



- vinyl esters of carboxylic acid, such as vinyl acetate, vinyl Versatate® and vinyl propionate;

- ethylenically unsaturated monocarboxylic and dicarboxylic acids, such as acrylic acid, methacrylic acid, itaconic acid, maleic acid and fumaric acid, and monoalkyl esters of dicarboxylic

- amides of unsaturated carboxylic acids, such as acrylamide, methacrylamide, N-methylolacrylamide or methacrylamide, and N-alkylacrylamides;

- amides of vinylamine, especially vinylformamide or vinylacetamide; and

- unsaturated ethylenic monomers containing a secondary, tertiary or quaternary amino group, or a heterocyclic group containing nitrogen, such as, for example, vinylpyridines, vinylimidazole, aminoalkyl (meth)acrylates and aminoalkyl (meth)acrylamides such

as dimethylaminoethyl (meth)acrylate, di-tert-butylaminoethyl (meth)acrylate and dimethylamino(meth)acrylamide. Likewise, it is possible to use zwitterionic monomers such as, for example, 5 sulphopropyl(dimethyl)aminopropyl acrylate.

In order to prepare the copolymers of formula (IA) or (IB) for which  $Y = H$  and  $Y' = NH_2$ , it is preferred to use as ethylenically unsaturated monomers the amides of vinylamine, for example vinylformamide or 10 vinylacetamide. The copolymer obtained is then hydrolysed to acid or basic pH.

In order to prepare the copolymers of formula (IA) or (IB) for which  $Y = H$  and  $Y' = OH$ , it is preferred to use as ethylenically unsaturated monomers 15 vinyl esters of carboxylic acid such as, for example, vinyl acetate. The copolymer obtained is then hydrolysed to acid or basic pH.

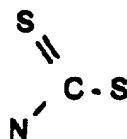
The types and amounts of copolymerizable monomers employed according to the present invention 20 vary depending on the particular final application for which the block polymer is intended. These variations are well known and may be easily determined by those skilled in the art.

In order for the polymer of general formula 25 (IA) or (IB) to be a block polymer, the **"precursor"** compound of general formula (IIA) or (IIB) must be a polymer. Thus,  $n$  is greater than or equal to 1, preferably greater than 5. The monomer units of this

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polymer may be identical or different.

The essential characteristic of the invention stems from the nature of this precursor of general formula (IIA) or (IIB). This precursor (IIA) or (IIB) forms part of the family of dithiocarbamates, the functional group of which is:



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In the case of copolymers of **formula (IA)** or of precursor polymers of **formula (IIA)**, the nitrogen atom of the dithiocarbamate functional group must form part of a ring and the other atoms of the said ring must exhibit an electron-withdrawing effect on the doublet of the nitrogen of the dithiocarbamate functional group.

The nature of this ring Z, comprising the nitrogen of the dithiocarbamate functional group, can vary, given that there is an electron-withdrawing effect on the doublet of the nitrogen.

On account of the process, the multiblock polymers of formula (IA) have the same characteristics with regard to the ring Z.

In compounds of formula (IA) and (IIA), the ring Z is a ring based on carbon atoms.

This carbocycle may include at least one heteroatom other than the nitrogen which links the ring

to  $-C(=S)-S-$ ; this heteroatom may be chosen from O, S, N and/or P. Preferably it is O or N.

The ring Z may be an aromatic or heteroaromatic ring.

- 5           The ring Z may be functionalized and comprise at least one of the following functional groups: carbonyl ( $C=O$ ),  $SO_2$ ,  $POR$ ,  $R$  representing an alkyl, aryl, OR, SR or  $NR_2$  group, where R represents an alkyl or aryl group, these being identical or different.

- 10   Preferably, the functionalized group is carbonyl.

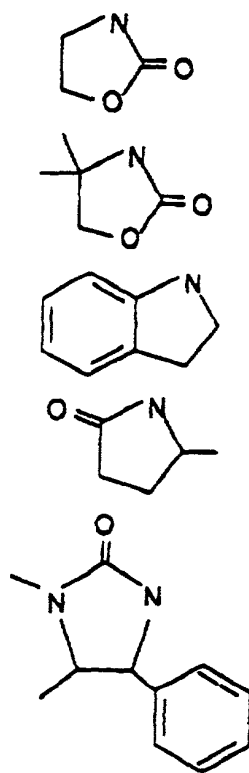
It is also preferable for the functionalized group to be directly linked to the nitrogen of the dithiocarbamate functional group.

- The ring Z may be substituted with at least
- 15   one of the following groups: alkyl, aryl, alkoxycarbonyl or aryloxycarbonyl ( $-COOR$ ), carboxyl ( $-COOH$ ), acyloxy ( $-O_2CR$ ), carbamoyl ( $-CONR_2$ ), cyano ( $-CN$ ), alkylcarbonyl, alkylarylcarbonyl, arylcarbonyl, arylalkylcarbonyl, phthalimido, maleimido, succinimido,
- 20   amidino, guanidino, hydroxyl ( $-OH$ ), amino ( $-NR_2$ ), halogen, allyl, epoxy, alkoxy ( $-OR$ ), S-alkyl, S-aryl, groups having a hydrophilic or ionic character, such as the alkali metal salts of carboxylic acids or the alkali metal salts of sulphonic acid, polyalkylene
- 25   oxide chains (PEO, PPO), cationic substituents (quaternary ammonium salts), R representing an alkyl or aryl group.

The ring Z may also be substituted with at

least one carbocycle or a heterocycle; this being optionally aromatic and/or substituted with one of the preceding groups. In the latter case, and according to a preferred variant, the ring Z and its cyclic substituent have two common atoms.

The ring Z is preferably chosen from one of the following rings:



Likewise, in the case of copolymers of **formula (IB)** or of precursor polymers of **formula (IIB)**, the nitrogen atom of the dithiocarbamate functional group must be linked to  $R^2$  and  $R^3$  groups, at least one of which induces a delocalizing or electron-withdrawing effect with respect to the electron density of the

nitrogen atom of the dithiocarbamate functional group.

According to a first variant,  $R^2$  and/or  $R^3$  exert a  $\pi$  withdrawing effect. For this purpose,  $R^2$  and/or  $R^3$  may represent a carbonyl or (hetero)aromatic group.

According to a second variant,  $R^2$  and/or  $R^3$  exert a  $\Sigma$  withdrawing effect. For this purpose,  $R^2$  and/or  $R^3$  may represent an alkyl group substituted with electron-withdrawing groups.

With regard to the substituent  $R^1$  of the compounds of formula (IA), (IB), (IIA) and (IIB), it preferably represents:

- a group of formula  $CR^{11}R^{12}R^{13}$ , in which:

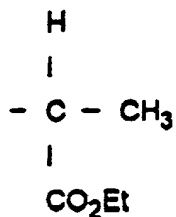
.  $R^{11}$ ,  $R^{12}$  and  $R^{13}$  represent groups (i), (ii)

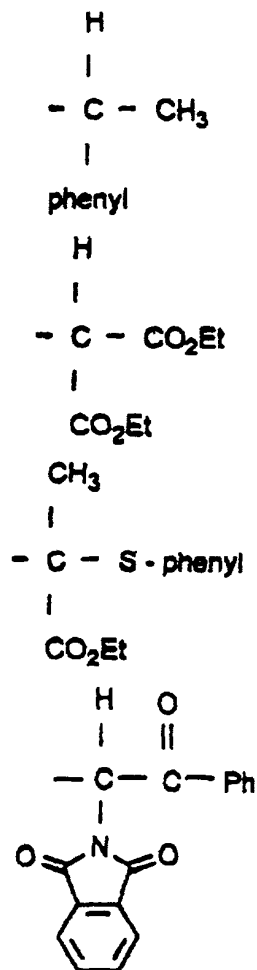
or (iii) as defined above, or

.  $R^{11} = R^{12} = H$  and  $R^{13}$  is an aryl, alkene or alkyne group,

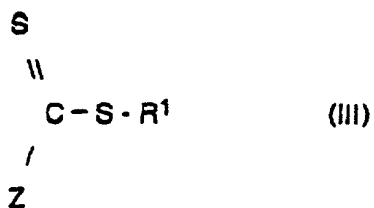
- or a  $-COR^{14}$  group in which  $R^{14}$  represents a group (i), (ii) or (iii) as defined above.

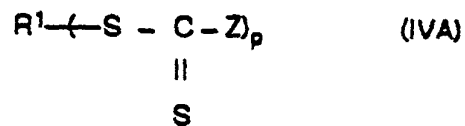
It may especially be chosen from the following groups:





5                   The precursor polymer of formula (IIA) may  
 come from the radical polymerization of an  
 ethylenically unsaturated monomer of formula:  
 $\text{CXX}' (= \text{CV} - \text{CV}')_n = \text{CH}_2$  by bringing the said monomer into  
 contact with a radical polymerization initiator and a  
 10 compound of general formula (IIIA) or (IVA):





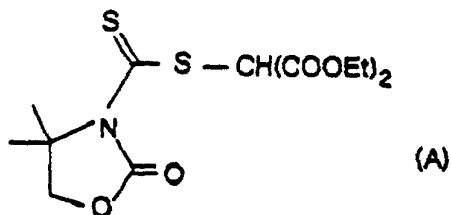
p being between 2 and 10, preferably between 2 and 5.

5 In the general formulae (IIIA) or (IVA), the symbols Z and  $R^1$  have the same meaning as previously. The preferences with regard to its symbols are the same as above.

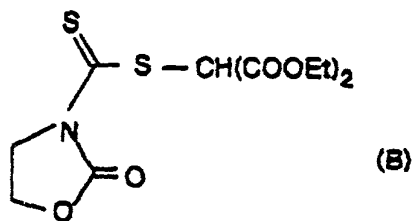
Among compounds of formula (IVA), when  $p = 2$ ,  
10  $R^1$  may be chosen from the groups -  $CH_2$  - phenyl -  $CH_2$  - or -  $(CH_2)_q$  -, where q is between 2 and 10.

According to the preferred variants, the compound of formula (IIIA) is chosen from those of the following formulae (A) to (E):

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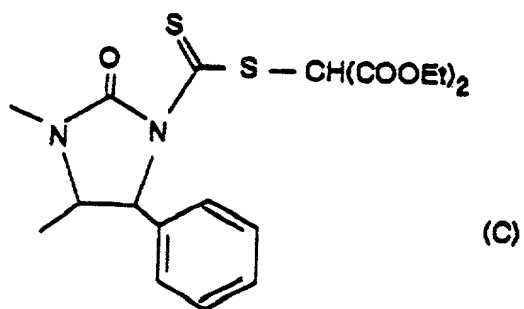
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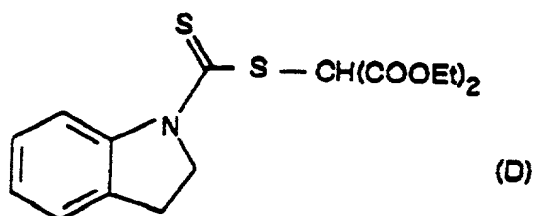
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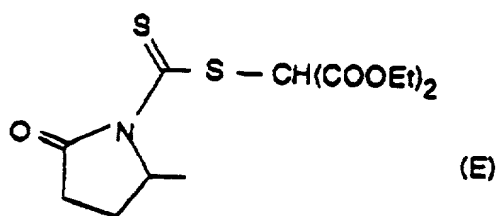
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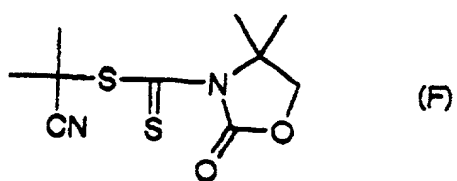
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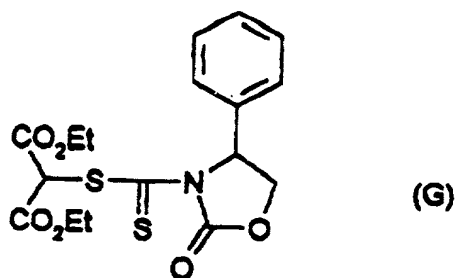
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CCOC(=O)C(S=C1N(C(=O)OCC)COC1=O)C(=O)OCC (H)

Likewise, the precursor compound of general formula (IIB) may come from the radical polymerization of an ethylenically unsaturated monomer of formula:  $CXX' (=CV-CV')_n=CH_2$ , during which the said monomer is brought into contact with a radical polymerization initiator and a compound of general formula (IIIB), (IVB) or (VB):

$$\text{R}^3\text{R}^2\text{N}-\text{C}(=\text{S})-\text{S}-\text{R}^1 \quad (\text{III B})$$
$$\text{R}^2\text{--}\text{N}\text{--}\left[\text{C}\begin{array}{l} \text{S} \\ \parallel \\ \text{S} \end{array}\text{--}\text{S}\text{--}\text{R}^1\right]_p \quad (\text{IVB})$$
$$\text{R}^1 - \text{S} - \text{C}(=\text{S}) - \text{N} - \text{R}^2 \bigg]_p \quad (\text{VB})$$

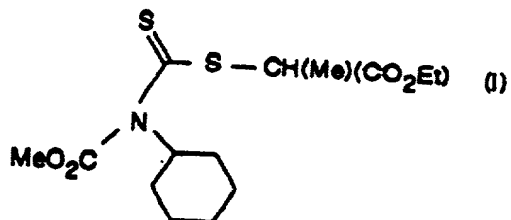
25 p being between 2 and 10.

In the general formulae (IIIB), (IVB) or (VB), the symbols  $R^1$ ,  $R^2$  and  $R^3$  have the same meaning as previously. The preferences with regard to its symbols

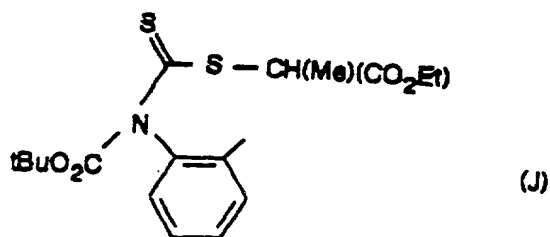
are the same as above.

According to the preferred variants, the compound of formula (IIIB) is chosen from the compounds of the following formulae:

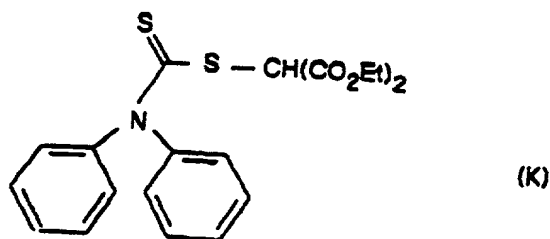
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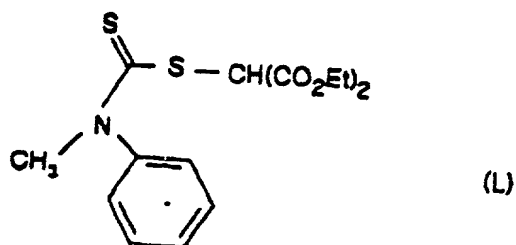
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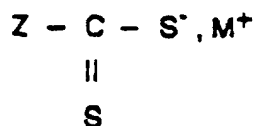
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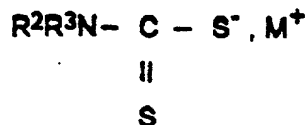
25

The compounds of formula (IIIA) or (IIIB) are generally obtained by the reaction of the corresponding

amine with CS<sub>2</sub>, so as to obtain the salts of formulae:



5 or



in which M represents sodium, potassium or  
10 lithium.

This salt is then brought into contact with a halogen-containing derivative Hal-R<sup>1</sup> (Hal represents Cl, Br or I) in order to give the precursor of formula (IIIA) or (IIIB).

15            During the synthesis of the precursor polymer of formula (IIA) or (IIB), the radical polymerization initiators and the ethylenically unsaturated monomers are of the type of those mentioned previously.

The complete process of synthesizing a block  
20 polymer of formula (IA) or (IB) according to the  
invention may therefore consist in:

(1) synthesizing a polymer by bringing into contact with each other an ethylenically unsaturated monomer of formula:  $CXX' (=CV-CV')_n=CH_2$ , a radical polymerization initiator and a compound of formula (IIIA), (IIIB), (IVA), (IVB) or (VB), and

(2) using this polymer obtained at step (1) as precursor of general formula (IIA) or (IIB) in order

to prepare a diblock polymer by bringing it into contact with a new ethylenically unsaturated monomer of formula:  $CYY' (=CW-CW')_n=CH_2$  and a radical polymerization initiator.

5                This step (2) may be repeated as many times as desired using new monomers to synthesize new blocks and to obtain a multiblock polymer.

As indicated previously, for the preparation of precursors of formula (IIA) or (IIB) for which  $X = H$  and  $X' = NH_2$ , it is preferred to use, as ethylenically unsaturated monomers, amides of vinylamine, for example vinylformamide or vinylacetamide. The polymer obtained is then hydrolysed to acid or basic pH.

Likewise, for the preparation of precursors of formula (IIA) or (IIB) for which  $X = H$  and  $X' = OH$ , it is preferred to use vinyl esters of carboxylic acids, such as vinyl acetate for example, as ethylenically unsaturated monomers. The polymer obtained is then hydrolysed to acid or basic pH.

20                According to this principle, the invention therefore also relates to a process for preparing multiblock polymers, in which the implementation of the process previously described is repeated at least once, using:

- 25                - different monomers from those of the previous implementation, and
- instead of the precursor compound of formula (IIA) or (IIB), the block polymer coming from

the previous implementation.

If the implementation is repeated once, a triblock polymer will be obtained, if it is repeated twice, a "quadriblock" polymer will be obtained, and so  
5 on. In this way, at each new implementation, the product obtained is a block polymer having an additional polymer block.

Therefore, in order to prepare multiblock polymers, the process consists in repeating, several  
10 times, the implementation of the preceding process on the block polymer coming from each previous implementation using different monomers.

According to this method of preparing multiblock polymers, when it is desired to obtain  
15 homogeneous block polymers without a composition gradient, and if all the successive polymerizations are carried out in the same reactor, it is essential for all the monomers used in one step to have been consumed before the polymerization of the next step starts,  
20 therefore before the new monomers are introduced.

The compounds of formula (IVA) and (IVB) are particularly advantageous as they allow a polymer chain to be grown on at least two active sites. With this type of compound, it is possible to save on  
25 polymerization steps in order to obtain an n-block copolymer.

Thus, if  $p = 2$ , the first block is obtained by the polymerization of a monomer M1 in the presence

of the compound of formula (IVA) or (IVB). This first block may then grow at each of its ends by the polymerization of a second monomer M2. A triblock copolymer is obtained. This triblock polymer itself may  
5 grow at each of its ends by the polymerization of a third monomer M3. Thus, a "pentablock" copolymer is obtained in only three steps.

If  $p$  is greater than 2, the process makes it possible to obtain homopolymers or block copolymers  
10 whose structure is "multi-branched" or hyperbranched.

The polymerization is carried out according to any method known to those skilled in the art. It may be carried out in bulk, in solution or in emulsion. The temperature may vary between ambient temperature and  
15 150°C, depending on the nature of the monomers used. The process is carried out in the absence of a UV source.

The process according to the invention has the advantage of resulting in block polymers having a  
20 low polydispersity index.

It also makes it possible to control the molecular mass of the polymers.

The invention therefore also relates to the block polymers which can be obtained by the above  
25 process.

In general, these polymers have a polydispersity index (PI) of at most 2, preferably of at most 1.5.

The preferred block polymers are those having at least two polymer blocks chosen from the following combinations:

- polystyrene/polymethyl acrylate,
- 5 - polystyrene/polyethyl acrylate,
- polystyrene/poly(*tert*-butyl acrylate),
- polyethyl acrylate/polyvinyl acetate,
- polybutyl acrylate/polyvinyl acetate,
- poly(*tert*-butyl acrylate)/polyvinyl acetate.

10           Finally, the process for synthesizing the precursor polymers of general formula (IIA) or (IIB) also makes it possible to synthesize polymers having a low polydispersity index. In general, these precursor polymers have a polydispersity index of at most 2,  
15 preferably of at most 1.5.

Preferably, for these precursor polymers of general formula (IIA) or (IIB),  $n$  is greater than or equal to 6.

20           The following examples illustrate the invention without, however, limiting the scope thereof.



**EXAMPLES****1. SYNTHESIS OF THE PRECURSOR COMPOUNDS OF FORMULA (IIIA) or (IIIB)**

5

**Example 1.1: Synthesis of dithiocarbamate of formula (A)**

Dissolved in a round-bottomed flask are  
10 17.8 g of 2-amino-2-methyl-1-propanol in 100 ml of a  
0.1M solution of sodium ethanolate in ethanol. Next,  
24 ml of diethyl carbonate are added and the solution  
obtained is stirred for 24 hours. The solvent is then  
evaporated. After drying, 17.26 g of 5,5-dimethyl-2-  
15 oxazolidone are obtained with a yield of 75%.

5.28 g of a 50% dispersion of sodium hydride  
are washed with pentane and added to this is a THF/DMSO  
mixture (100 ml THF/100 ml DMSO). This solution is  
cooled to 0°C and added to it are 11.5 g of 5,5-  
20 dimethyl-2-oxazolidone obtained from the first step.  
The cooling system is interrupted and the reaction  
mixture is stirred for 1 h 30 minutes and then a white  
precipitate appears. The temperature is again lowered  
to 0°C and 1 equivalent of CS<sub>2</sub> (7.6 g) is added. The  
25 solution turns a red colour and the stirring is  
continued until the reaction mixture is perfectly clear  
(approximately 3 hours). The solution is then taken up  
in water and extracted with dichloromethane.

The aqueous phase is recovered and added to this are 50 ml of ethanol and 16.2 ml of diethyl chloromalonate. Stirring continues overnight at room temperature and the yellow solution obtained is concentrated in vacuo before being taken up in a saturated aqueous sodium chloride solution. Finally, it is extracted with ether.

7.9 g of dithiocarbamate of formula (A) are isolated by column chromatography. The yield is 23%.

10

**Example 1.2: Synthesis of dithiocarbamate of formula (B)**

2.6 g of a 50% dispersion of sodium hydride are washed with pentane and then introduced into a THF/DMSO mixture (200 ml THF / 200 ml DMSO). Next, 4.35 g of oxazolidone are added and the solution is stirred for an hour at room temperature. A white precipitate appears.

The reaction mixture is then cooled to  $-20^{\circ}\text{C}$  and 3.6 ml of  $\text{CS}_2$  are added. The solution turns orange and is stirred for 10 minutes at  $-20^{\circ}\text{C}$  and then for 2 hours at  $0^{\circ}\text{C}$ . The reaction mixture is again cooled to  $-20^{\circ}\text{C}$  and 4 ml of diethyl chloromalonate are added. The solution is stirred for 10 minutes at  $-20^{\circ}\text{C}$ , 1 hour at  $0^{\circ}\text{C}$  and 1 hour at room temperature.

The reaction mixture is taken up in ether and

the organic phase is washed with water and then with a saturated sodium chloride solution.

2.6 g of dithiocarbamate of formula (B) are isolated by column chromatography. The yield is 23%.

5

**Example 1.3: Synthesis of dithiocarbamate of formula (C)**

66 g of ephedrine are mixed with 72 g of  
10 urea. The mixture is heated at 170°C for 30 minutes and  
then at 200°C for 2 hours. After cooling to room  
temperature, 200 ml of water are added. The white  
precipitate which forms is filtered and washed with a  
5% aqueous hydrochloric acid solution and then  
15 recrystallized in ethanol. 28 g of 1,5-dimethyl-4-  
phenyl-2-imidazolidone are obtained with a yield of  
37%.

2.6 g of a 50% dispersion of sodium hydride  
are washed with pentane and a THF/DMSO mixture (200 ml  
20 THF / 200 ml DMSO) is added. 9.5 g of 1,5-dimethyl-4-  
phenyl-2-imidazolidone obtained previously are added  
and the solution is stirred for 1 hour at room  
temperature. The reaction mixture is then cooled to 0°C  
and 3 ml of CS<sub>2</sub> are added. The solution turns orange and  
25 is stirred at 0°C for 2 hours. The reaction mixture is  
taken up in 100 ml of water and extracted with  
dichloromethane.

The aqueous phase is recovered and 100 ml of ethanol and then 4 ml of diethyl chloromalonate are added. Stirring continues for 2 hours and the reaction mixture is taken up in ethyl acetate. The organic phase  
5 thus obtained is washed with water and then with a saturated sodium chloride solution before being concentrated in vacuo.

4.5 g of dithiocarbamate of formula (C) are isolated by column chromatography. The yield is 42%.

10

**Example 1.4: Synthesis of dithiocarbamate of formula (D)**

2.6 g of a 50% dispersion of sodium hydride  
15 are washed with pentane and then a THF/DMSO mixture (50 ml THF / 50 ml DMSO) is added. Next, 5.5 ml of indoline are added to the mixture and the solution is stirred for 1 hour at room temperature.

It is then cooled to 0°C and 3.6 ml of CS<sub>2</sub> are  
20 added. The solution turns orange and is stirred at 0°C for 2 hours. The reaction mixture is taken up in 100 ml of water and washed with dichloromethane.

The aqueous phase is recovered and 100 ml of ethanol and 6.4 ml of diethyl chloromalonate are added.  
25 The solution is stirred for 2 hours and then taken up in ether. The organic phase thus obtained is washed with water and then with a saturated sodium chloride solution before being concentrated.

11 g of dithiocarbamate of formula (D) are isolated by column chromatography in the form of yellow crystals. The yield is 79%.

5           **Example 1.5: Synthesis of dithiocarbamate of formula (E)**

1 g of 5-methyl-2-pyrrolidinone is added to 20 ml of a 1/1 THF/DMSO mixture. 0.56 g of potassium  
10 hydroxide and then 1 ml of water and 0.6 ml of CS<sub>2</sub> are added to the solution. The reaction mixture is stirred for 1 hour; the solution turns reddish black.

It is cooled to 0°C and 1 ml of diethyl  
chloromalonate is added. Stirring is continued for 30  
15 minutes at 0°C and then for 2 hours at room temperature. The reaction mixture is taken up in water and extracted with ethyl acetate. The organic phase is recovered and washed with water and then with a  
concentrated sodium chloride solution before being  
20 concentrated in vacuo.

0.86 g of dithiocarbamate of formula (E) is isolated by column chromatography in the form of a yellow oil. The yield is 26%.

25           **Example 1.6: Synthesis of dithiocarbamate of formula (F)**

1.76 g of a 50% dispersion of NaH (30 mmol)

5           After 1 h 30 min., a white precipitate is formed. The mixture is cooled to 0°C and CS<sub>2</sub> is then added. The solution turns red and stirring continues until the solution is clear (3 hours).

After stirring for 2 hours at room temperature, the solution obtained is yellow; it is concentrated in vacuo before being diluted in a saturated NaCl solution and extracted with ether.

2 g of dimer (5.2 mmol) are dissolved in 10 ml of 1,2-dichloroethane. 1.12 g (6.8 mmol) of AIBN are added and the solution is heated at reflux under argon for 6 hours. The solvent is then evaporated and the crude reaction product is purified by column chromatography (dichloromethane/heptane in a ratio of 9/1 and then 7/3). 2.34 g of dithiocarbamate of formula (F) are obtained, i.e. a yield of 33%.

**Example 1.7: Synthesis of dithiocarbamate of formula (G)**

6.8 g of phenylglycinol (50 mmol) are  
5 dissolved in a round-bottomed flask containing 50 ml of  
a 0.2M solution of EtONa in ethanol (prepared by adding  
10 mmol of NaH to 50 ml of ethanol). Added to this  
solution are 6 ml of diethyl carbonate (50 mmol). The  
solution is stirred for 24 hours and the solvent is  
10 then evaporated. The residue is diluted using a  
saturated aqueous NaCl solution and extracted with  
ethyl acetate.

After drying and evaporation, the crude  
reaction product is purified by column chromatography  
15 (dichloromethane/ethyl acetate in a ratio of 95/5).  
4.6 g of oxazolidinone are obtained, i.e. a yield of  
56%.

0.53 g of a 50% dispersion of NaH (11 mmol)  
is washed with pentane and then 20 ml of THF and 20 ml  
20 of DMSO are added. Next, 1.6 g of oxazolidinone  
(10 mmol) are added. After 30 minutes of reaction,  
200 ml of ether are added, causing two phases to form.  
The supernatant phase is removed and the residue is  
taken up in acetone and then precipitated by adding  
25 ether. The supernatant phase is again removed.

100 ml of acetone are added to the residue,  
followed by 1.12 ml (7 mmol) of diethyl chloromalonate.  
After 3 hours of stirring at room temperature, the

yellow solution obtained is concentrated in vacuo. Next, it is diluted in a saturated NaCl solution and then extracted with ether.

The crude reaction product is purified by column chromatography (heptane/ethyl acetate in a ratio of 7/3); 0.94 g of dithiocarbamate of formula (G) is isolated. The yield is 33%.

**Example 1.8: Synthesis of dithiocarbamate of formula (H)**

15.5 g of serine methyl ester hydrochloride (100 mmol) are dissolved in a round-bottomed flask containing 140 ml of water. 10.5 g of  $\text{KHCO}_3$  (105 mmol) are added and then, after 10 minutes, 14.6 g of  $\text{K}_2\text{CO}_3$  are added. The solution is cooled to  $0^\circ\text{C}$  and then 70 ml of phosgene (133 mmol of a 1.9M solution in toluene) are slowly added over 20 minutes. The solution is stirred overnight at room temperature. Two phases are obtained which are separated; the aqueous phase is evaporated and the residue is taken up in ethyl acetate. The organic phase is concentrated in order to give 14.3 g of intermediate oxazolidinone, i.e. a yield of 99%.

1.45 g of oxazolidinone (10 mmol) are dissolved in 20 ml of DMF and then 1.2 ml (20 mmol) of  $\text{CS}_2$  are added. The solution is cooled to  $0^\circ\text{C}$  and then 0.48 g (10 mmol) of NaH is added. The solution is



stirred for 30 minutes at 0°C and then for 30 minutes at room temperature. It is again cooled to 0°C and 0.8 ml (5 mmol) of diethyl chloromalonate is added to it. After stirring for 30 minutes at 0°C and then for 5 30 minutes at room temperature, the solution is diluted in ethyl acetate. Next, it is washed with water and then with brine. The organic phase is concentrated in vacuo. The crude reaction product is purified by column chromatography (heptane/ethyl acetate in a ratio of 10 7/3); 1.2 g of dithiocarbamate of formula (H) are isolated. The yield is 64%.

**Example 1.9: Synthesis of dithiocarbamate of formula (I)**

15

4.6 ml of cyclohexylamine (40 mmol) dissolved in 40 ml of ethyl ether are introduced into a round-bottomed flask and then 5.5 ml of triethylamine (40 mmol) and 3.5 ml (45 mmol) of methyl chloroformate 20 are added. After three hours of reaction, the solution is hydrolysed by adding water, the organic phase is washed with a saturated 1N HCl solution of NaHCO<sub>3</sub> and then with brine. The organic phase is dried over magnesium sulphate and concentrated in vacuo in order 25 to give 5.9 g (94%) of intermediate carbamate.

1.57 g (10 mmol) of this intermediate carbamate are dissolved in 20 ml of DMF and 1.2 ml (20 mmol) of CS<sub>2</sub> are then added. The solution is cooled

to 0°C and 0.48 g (10 mmol) of a 50% dispersion of NaH is added. After one hour at 0°C, the solution containing the sodium salt is added to a solution of 1.24 ml (9.5 mmol) of ethyl 2-bromopropionate in 20 ml of DMF at 0°C.

After stirring for two hours at room temperature, a yellow solution is obtained which is diluted by adding ethyl ether and hydrolysed by adding water. The organic phase is washed with water and then with brine before being dried and concentrated in vacuo.

The crude reaction product is purified by column chromatography (heptane/ethyl acetate in a ratio of 9/1); 1.6 g of dithiocarbamate of formula (I) are isolated. The yield is 50%.

**Example 1.10: Synthesis of dithiocarbamate of formula (J)**

0.58 g (3 mmol) of intermediate carbamate (prepared from o-toluidine and (Boc)<sub>2</sub>O (di-tert-butyl dicarbonate)) is dissolved in 10 ml of DMF and then 0.35 ml (6 mmol) of CS<sub>2</sub> is added. The solution is cooled to 0°C and 0.144 g (3 mmol) of a 50% dispersion of NaH is added. After one hour at 0°C, the solution containing the sodium salt is slowly added to a solution of 0.39 ml (3 mmol) of ethyl 2-bromopropionate

in 10 ml of DMF at 0°C.

After stirring for 2 hours at room temperature, the yellow solution obtained is diluted by adding ethyl ether and hydrolysed by adding water. The organic phase is washed with water and then with brine before being dried and concentrated in vacuo.

The crude reaction product is column purified (heptane/ethyl acetate in a ratio of 9/1); 0.68 g of dithiocarbamate of formula (J) is isolated. The yield is 61%.

**Example 1.11: Synthesis of dithiocarbamate of formula (K)**

1.3 equivalents of NaH (1.24 g; 26 mmol) are suspended in 10 ml of THF in a round-bottomed flask placed under argon. 1 equivalent of diphenylamine (3.38 g; 20 mmol) dissolved in a mixture of 18 ml of DMSO and 9 ml of THF is added at 0°C. The colour turns a pale green.

After stirring for one hour, 2.36 equivalents of CS<sub>2</sub> (2.84 ml; 47.2 mmol) are added and the solution becomes orangey yellow. After stirring for 30 minutes, the solution is cooled to -20°C and 1 equivalent of a chlorinated agent (3.20 ml; 20 mmol) is added. The solution is stirred for two hours at room temperature. Next, it is hydrolysed, extracted with ethyl ether and then dried over magnesium sulphate and concentrated in

The product is isolated. It is in the form of a beige solid (melting point: 65°C). The yield is 85% without purification.

**Example 1.12: Synthesis of dithiocarbamate of formula (L)**

After stirring for one hour, 2.36 equivalents of CS<sub>2</sub> (2.84 ml; 47.2 mmol) are added at 0°C. The solution then becomes brownish red. After stirring for 30 minutes, the solution is cooled to -15°C and 1  
20 equivalent of a chlorinated agent (3.20 ml; 20 mmol) is added. The solution becomes brownish yellow; it is stirred for 2 hours at room temperature. Next, it is hydrolysed, extracted with ethyl ether, then dried over magnesium sulphate and concentrated in vacuo.

25                    After purification by column chromatography  
                      (heptane/ethyl acetate: 9/1), 4.42 g of product are  
                      isolated. It is in the form of a yellow oil. The yield  
                      is 70%.

## 2. PREPARATION OF HOMOPOLYMERS of formula (IIA) or (IIB)

These examples demonstrate that the radical  
 5 polymerization is controlled by the use of precursors  
 of general formula (III). The control character of the  
 reaction appears through the values of the  
 polydispersity indices  $PI = M_w/M_n$ , which are less than  
 1.5, and the values of the number-average molecular  
 10 mass  $M_n$ , which are close to the theoretical values and  
 expressed by the following formula:

$$M_n = \frac{M_m \cdot x}{M_p \cdot 100} M_{mol}$$

where:  $M_m$ : moles of monomer  
 $M_p$ : moles of precursor of formula (III)  
 $x$ : conversion of the monomer (%)  
 15  $M_{mol}$ : molecular mass of the monomer (g/mol).

### **Example 2.1: Styrene homopolymer**

Introduced into a 10 ml round-bottomed flask  
 are:

- 20 - 1 mmol of dithiocarbamate of formula (A)  
 (0.35 g) and  
 - 40 mmol of styrene (4.16 g).

The temperature is raised to 95°C and  
 0.03 mmol of lauroyl peroxide (12.8 mg) is added. The  
 25 polymerization lasts 12 hours, during which 0.02 mmol

of lauroyl peroxide is added every two hours.

The polymer is recovered by evaporating the traces of residual monomer and analysed by GPC in a THF medium and in polystyrene equivalents.

5 GPC analysis of the homopolymer obtained above allows its number-average mass  $M_n$  to be measured. It also allows its weight-average mass ( $M_w$ ) to be measured and hence the polydispersity index (PI), corresponding to the ratio of  $M_w$  to  $M_n$ .

10 The results are as follows:

- degree of conversion: 43%,
- average molecular mass  $M_n = 3500$ ,
- polydispersity index  $PI = 1.1$ .

15 **Example 2.2: methyl acrylate homopolymer**

Introduced into a round-bottomed flask are:

- 1 mmol of dithiocarbamate of formula (A)
- (0.35 g) and

20 - 40 mmol of methyl acrylate (3.44 g).

The temperature is raised to 80°C and 0.03 mmol of lauroyl peroxide (12.8 mg) is added. The polymerization lasts 6 hours during which 0.02 mmol of lauroyl peroxide is added every two hours.

25 The polymer is recovered by evaporating, under vacuum, the traces of residual monomer and analysed by GPC in THF medium and in polystyrene equivalents:

- degree of conversion: 77%,
- average molecular mass  $M_n = 3000$ ,
- polydispersity index  $PI = 1.1$ .

5                    **Example 2.3: styrene homopolymer /**  
**polymerization kinetics**

A stock solution is prepared by mixing:

- 5.504 g of styrene,
- 10        - 0.231 g of dithiocarbamate of formula (A)

and

- 11.4 mg of azobis(isobutyronitrile) (AIBN).

Aliquots of about 0.9 g of this solution are  
dispensed in tubes and heated to 70°C. The  
15        polymerization in the various tubes is stopped at  
different times by cooling and introducing 4 ml of  
toluene containing 25 mg of hydroquinone.

For each tube, the polymer is recovered by  
evaporating the toluene and the residual monomer; it is  
20        analysed by GPC in THF medium. The masses are given in  
polystyrene equivalents. The results obtained are given  
in Table 1.

Table 1

Time (min.)	Conversion (%)	$M_n$	PI
63	6.6	770	(*)
126	14.4	1260	(*)
240	27.4	1700	1.2
359	37.2	2200	1.2
1443	80.0	4400	1.2

(\*): part of the mass distribution is outside the calibration; the polydispersity index for these 5 specimens cannot therefore be calculated.

**Example 2.4: ethyl acrylate homopolymer / polymerization kinetics**

10 A stock solution is prepared by mixing:

- 5.533 g of ethyl acrylate,
- 0.241 g of dithiocarbamate of formula (A)

and

- 11.3 mg of azobis(isobutyronitrile) (AIBN).

15 Aliquots of about 10 g of this solution are dispensed in tubes and heated to 70°C. The polymerizations in tubes are stopped at different times by cooling and introducing 4 ml of toluene containing 25 mg of hydroquinone.



For each tube, the polymer is recovered by evaporating the toluene and the residual monomer; it is analysed by GPC in THF medium. The masses are given in polystyrene equivalents. The results obtained are given in Table 2.

Table 2

Time (min.)	Conversion (%)	$M_n$	PI
31	1.9	323	(*)
49	15.6	2100	1.7
101	50.6	4300	1.6
150	63.5	5300	1.5
211	77.2	5900	1.6

(\*): part of the mass distribution is outside the calibration; the polydispersity index for this specimen cannot therefore be calculated.

#### Example 2.5: styrene homopolymer

Introduced into a round-bottomed flask are:

- 2.23 g of styrene,
- 84.5 mg of dithiocarbamate of formula (B)

and

- 4.2 mg of lauroyl peroxide.

The temperature is raised to 110°C. The reaction lasts 24 hours during which several additions

of lauroyl peroxide are made:

- 4.7 mg after 2 hours,
- 4.1 mg after 4 hours.

The polymer is recovered by evaporating,  
5 under vacuum, the traces of residual monomer and  
analysed by GPC in THF medium and in polystyrene  
equivalents:

- degree of conversion: 98.1%,
- average molecular mass  $M_n = 8500$ ,
- 10 - polydispersity index  $PI = 1.3$ .

**Example 2.6: ethyl acrylate homopolymer**

Introduced into a round-bottomed flask are:  
15 - 2.13 g of ethyl acrylate,  
- 84.5 mg of dithiocarbamate of formula (B)

and

- 4.5 mg of lauroyl peroxide.

The temperature is raised to 80°C. The  
20 reaction lasts 24 hours during which several additions  
of lauroyl peroxide are made:

- 5.0 mg after 2 hours,
- 3.8 mg after 4 hours.

The polymer is recovered by evaporating,  
25 under vacuum, the traces of residual monomer and  
analysed by GPC in THF medium and in polystyrene  
equivalents:

- degree of conversion: 97.5%,
- average molecular mass  $M_n = 10,700$ ,
- polydispersity index  $PI = 1.2$ .

5

**Example 2.7: vinyl acetate homopolymer**

Introduced into a round-bottomed flask are:

- 1.82 g of vinyl acetate,
- 85.1 mg of dithiocarbamate of formula (B)

10 and

- 8.8 mg of lauroyl peroxide.

The temperature is raised to 80°C. The reaction lasts 24 hours during which several additions of lauroyl peroxide are made:

15

- 8.1 mg after 2 hours,
- 8.0 mg after 4 hours.

The polymer is recovered by evaporating, under vacuum, the traces of residual monomer and analysed by GPC in THF medium and in polystyrene

20 equivalents:

- degree of conversion: 59.2%,
- average molecular mass  $M_n = 4600$ ,
- polydispersity index  $PI = 2.0$ .

25

**Example 2.8: styrene homopolymer**

Introduced into a round-bottomed flask are:

- 2.24 g of styrene,
- 0.113 g of dithiocarbamate of formula (C)

and

- 4.5 mg of lauroyl peroxide.

5           The temperature is raised to 110°C. The reaction lasts 24 hours during which several additions of lauroyl peroxide are made:

- 4.7 mg after 2 hours,
- 3.6 mg after 4 hours.

10           The polymer is recovered by evaporating, under vacuum, the traces of residual monomer and analysed by GPC in THF medium and in polystyrene equivalents:

- degree of conversion: 98.0%,
- 15           - average molecular mass  $M_n = 7600$ ,
- polydispersity index  $PI = 1.6$ .

#### **Example 2.9: ethyl acrylate homopolymer**

20           Introduced into a round-bottomed flask are:

- 2.13 g of ethyl acrylate,
- 0.115 g of dithiocarbamate of formula (C)

and

- 4.3 mg of lauroyl peroxide.

25           The temperature is raised to 80°C. The reaction lasts 24 hours during which several additions of lauroyl peroxide are made:

- 4.6 mg after 2 hours,
- 4.9 mg after 4 hours.

The polymer is recovered by evaporating, under vacuum, the traces of residual monomer and analysed by GPC in THF medium and in polystyrene equivalents:

- degree of conversion: 95.2%,
- average molecular mass  $M_n = 8600$ ,
- polydispersity index  $PI = 1.4$ .

10

**Example 2.10: vinyl acetate homopolymer**

Introduced into a round-bottomed flask are:

- 1.84 g of vinyl acetate,
- 0.112 g of dithiocarbamate of formula (C)

and

- 8.3 mg of lauroyl peroxide.

The temperature is raised to 80°C. The reaction lasts 24 hours during which several additions of lauroyl peroxide are made:

20

- 8.8 mg after 2 hours,
- 8.0 mg after 4 hours.

The polymer is recovered by evaporating, under vacuum, the traces of residual monomer and analysed by GPC in THF medium and in polystyrene equivalents:

25

- degree of conversion: 33%,

- average molecular mass  $M_n = 2500$ ,
- polydispersity index  $PI = 1.4$ .

**Example 2.11: styrene homopolymer**

5

Introduced into a round-bottomed flask are:

- 2.23 g of styrene,
- 95.1 mg of dithiocarbamate of formula (D)

and

10

- 4.1 mg of lauroyl peroxide.

The temperature is raised to 110°C. The reaction lasts 24 hours during which several additions of lauroyl peroxide are made:

15

- 4.2 mg after 2 hours,
- 3.9 mg after 4 hours.

The polymer is recovered by evaporating, under vacuum, the traces of residual monomer and analysed by GPC in THF medium and in polystyrene equivalents:

20

- degree of conversion: 97.6%,
- average molecular mass  $M_n = 6800$ ,
- polydispersity index  $PI = 2.0$ .

**Example 2.12: ethyl acrylate homopolymer**

25

Introduced into a round-bottomed flask are:

- 2.15 g of ethyl acrylate,

- 98.7 mg of dithiocarbamate of formula (D)

and

- 4.1 mg of lauroyl peroxide.

The temperature is raised to 80°C. The

5 reaction lasts 24 hours during which several additions of lauroyl peroxide are made:

- 4.5 mg after 2 hours,
- 4.1 mg after 4 hours.

The polymer is recovered by evaporating,

10 under vacuum, the traces of residual monomer and analysed by GPC in THF medium and in polystyrene equivalents:

- degree of conversion: 91.8%,
- average molecular mass  $M_n = 7900$ ,
- 15 - polydispersity index  $PI = 1.6$ .

#### **Example 2.13: styrene homopolymer**

Introduced into a round-bottomed flask are:

- 20
- 2.23 g of styrene,
  - 87 mg of dithiocarbamate of formula (E) and
  - 4.0 mg of lauroyl peroxide.

The temperature is raised to 110°C. The

reaction lasts 24 hours during which several additions  
25 of lauroyl peroxide are made:

- 4.6 mg after 2 hours,
- 4.6 mg after 4 hours.





**Example 2.15: vinyl acetate homopolymer**

Introduced into a round-bottomed flask are:

- 1.83 g of vinyl acetate,
- 5        - 97.4 mg of dithiocarbamate of formula (E)

and

- 8.1 mg of lauroyl peroxide.

The temperature is raised to 80°C. The  
reaction lasts 24 hours during which several additions  
10 of lauroyl peroxide are made:

- 8.5 mg after 2 hours,
- 8.3 mg after 4 hours.

The polymer is recovered by evaporating,  
under vacuum, the traces of residual monomer and  
15 analysed by GPC in THF medium and in polystyrene  
equivalents:

- degree of conversion: 23.4%,
- average molecular mass  $M_n = 2100$ ,
- polydispersity index  $PI = 1.35$ .

20

**Example 2.16: vinyl acetate homopolymer**

Introduced into a glass tube are:

- 0.015 mmol of AIBN (2.4 mg),
- 25        - 10 mmol of ethyl acrylate (1 g) and
- 0.13 mmol of dithiocarbamate of formula (F)  
(33.8 mg).

The tube is closed by a screw stopper and

then immersed in an oil bath preheated to 80°C. The polymerization lasts 24 hours.

The polymer is recovered by evaporating the traces of residual monomer and analysed by GPC in THF medium and in polystyrene equivalents. The results obtained are as follows:

- degree of conversion: 61%,
- number-average molar mass  $M_n = 5600$ ,
- polydispersity index  $PI = 1.4$ .

10

**Example 2.17: styrene homopolymer**

Introduced into a glass tube are:

15

- 0.014 mmol of AIBN (2.3 mg),
- 10 mmol of styrene (1.03 g) and
- 0.12 mmol of dithiocarbamate of formula (F) (32 mg).

The tube is closed by a screw stopper and then immersed in an oil bath preheated to 115°C. The polymerization lasts 24 hours.

20

The polymer is recovered by evaporating the traces of residual monomer and analysed by GPC in THF medium and in polystyrene equivalents. The results obtained are as follows:

25

- degree of conversion: 95%,
- number-average molar mass  $M_n = 7200$ ,
- polydispersity index  $PI = 1.19$ .

**Example 2.18: methyl methacrylate homopolymer**

Introduced into a glass tube are:

- 0.012 mmol of AIBN (2 mg),
- 5       - 10 mmol of ethyl acrylate (1 g),
- 0.12 mmol of dithiocarbamate of formula (F)  
(31.7 mg) and
- 1 g of methyl ethyl ketone.

The tube is closed by a screw stopper and  
10 then immersed in an oil bath preheated to 80°C. The  
polymerization lasts 24 hours.

The polymer is recovered by evaporating the  
traces of residual monomer and analysed by GPC in THF  
medium and in polystyrene equivalents. The results  
15 obtained are as follows:

- degree of conversion: 96%,
- number-average molar mass  $M_n = 13,900$ ,
- polydispersity index  $PI = 1.64$ .

**20       Example 2.19: vinyl acetate homopolymer**

Introduced into a glass tube are:

- 0.026 mmol of AIBN (2 mg),
- 10 mmol of vinyl acetate (0.86 g) and
- 25       - 0.12 mmol of dithiocarbamate of formula (G)  
(48 mg).

The tube is closed by a screw cock and then  
immersed in an oil bath preheated to 80°C. The

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**Example 2.21: styrene homopolymer**

Introduced into a glass tube are:

- 0.013 mmol of AIBN (2.1 mg),
- 5        - 10 mmol of styrene (1.04 g) and
- 0.12 mmol of dithiocarbamate of formula (G)  
(48 mg).

The tube is closed by a screw stopper and  
then immersed in an oil bath preheated to 115°C. The  
10 polymerization lasts 24 hours.

The polymer is recovered by evaporating the  
traces of residual monomer and analysed by GPC in THF  
medium and in polystyrene equivalents.

- degree of conversion: 95%,
- 15        - number-average molar mass  $M_n = 5300$ ,
- polydispersity index  $PI = 1.28$ .

**Example 2.22: vinyl acetate homopolymer**

20        Introduced into a glass tube are:

- 0.026 mmol of AIBN (4.2 mg),
- 10 mmol of vinyl acetate (0.86 g) and
- 0.13 mmol of dithiocarbamate of formula (H)  
(48 mg).

25        The tube is closed by a screw stopper and  
then immersed in an oil bath preheated to 80°C. The  
polymerization lasts 24 hours.

The polymer is recovered by evaporating the traces of residual monomer and analysed by GPC in THF medium and in polystyrene equivalents. The results are as follows:

- 5                   - degree of conversion: 60%,  
                  - number-average molar mass  $M_n = 4700$ ,  
                  - polydispersity index  $PI = 1.91$ .

**Example 2.23: ethyl acrylate homopolymer**

10

Introduced into a glass tube are:

- 0.013 mmol of AIBN (2.1 mg),  
                  - 10 mmol of ethyl acrylate (1 g) and  
                  - 0.13 mmol of dithiocarbamate of formula (H)  
15 (48 mg).

The tube is closed by a screw stopper and then immersed in an oil bath preheated to 80°C. The polymerization lasts 24 hours.

The polymer is recovered by evaporating the  
20 traces of residual monomer and analysed by GPC in THF medium and in polystyrene equivalents. The results are as follows:

- degree of conversion: 72%,  
                  - number-average molar mass  $M_n = 6000$ ,  
25                   - polydispersity index  $PI = 1.48$ .

**Example 2.24: styrene homopolymer**

Introduced into a glass tube are:

- 0.013 mmol of AIBN (2.1 mg),
  - 5        - 10 mmol of styrene (1.04 g) and
  - 0.12 mmol of dithiocarbamate of formula (H)
- (48 mg).

The tube is closed by a screw stopper and then immersed in an oil bath preheated to 110°C. The

10 polymerization lasts 24 hours.

The polymer is recovered by evaporating the traces of residual monomer and analysed by GPC in THF medium and in polystyrene equivalents. The results are as follows:

- 15        - degree of conversion: 87%,
- number-average molar mass  $M_n$  = 8200,
- polydispersity index PI = 1.23.

**Example 2.25: vinyl acetate homopolymer**

20

Introduced into a glass tube are:

- 0.003 mmol of AIBN (0.6 mg),
  - 10 mmol of vinyl acetate (1 g) and
  - 0.14 mmol of dithiocarbamate of formula (I)
- 25        (48 mg).

The tube, connected to a vacuum line, is dipped into liquid nitrogen and then three "freezing/vacuum/return to ambient" cycles are carried

out on the contents of the tube so as to degas it. Next, it is vacuum sealed. After returning to ambient, it is immersed in an oil bath preheated to 80°C. The polymerization lasts 28 hours.

5           The polymer is recovered by opening the tube and then evaporating the traces of residual monomer. It is analysed by GPC in THF medium and in polystyrene equivalents. The results are as follows:

- degree of conversion: 6.6%
- 10           - number-average molar mass  $M_n = 890$
- polydispersity index  $PI = 1.24$ .

**Example 2.26: ethyl acrylate homopolymer**

15           Introduced into a glass tube are:

- 0.003 mmol of AIBN (0.6 mg),
- 10 mmol of ethyl acrylate (1 g) and
- 0.13 mmol of dithiocarbamate of formula (I)

(42 mg).

20           After the tube has been filled, it is degassed and vacuum sealed in a manner similar to Example 2.25. The polymerization lasts 64 hours at 80°C.

25           The polymer is recovered by evaporating the traces of residual monomer and analysed by GPC in THF medium and in polystyrene equivalents. The results are as follows:



- degree of conversion: 69%
- number-average molar mass  $M_n = 9500$
- polydispersity index  $PI = 1.2$ .

5      **Example 2.27: styrene homopolymer**

Introduced into a glass tube are:

- 9.6 mmol of styrene (1 g) and
  - 0.12 mmol of dithiocarbamate of formula (I)
- 10    (40.2 mg).

After the tube has been filled, it is degassed and vacuum sealed in a manner similar to Example 2.25. The polymerization lasts 72 hours at 110°C.

- 15      The polymer is recovered by evaporating the traces of residual monomer and analysed by GPC in THF medium and in polystyrene equivalents. The results are as follows:

- degree of conversion: 70%
- 20      - number-average molar mass  $M_n = 6200$
- polydispersity index  $PI = 1.14$ .

**Example 2.28: vinyl acetate homopolymer**

25      Introduced into a glass tube are:

- 0.003 mmol of AIBN (0.6 mg),
- 10 mmol of vinyl acetate (1 g) and

- 0.15 mmol of dithiocarbamate of formula (J)  
(56 mg).

After the tube has been filled, it is  
degassed and vacuum sealed in a manner similar to

5 Example 2.25. The polymerization lasts 27 hours at  
80°C.

The polymer is recovered by evaporating the  
traces of residual monomer and analysed by GPC in THF  
medium and in polystyrene equivalents. The results are

10 as follows:

- degree of conversion: 25.7%
- number-average molar mass  $M_n = 2200$
- polydispersity index  $PI = 1.66$ .

15 **Example 2.29: ethyl acrylate homopolymer**

Introduced into a glass tube are:

- 0.003 mmol of AIBN (0.6 mg),
- 10 mmol of ethyl acrylate (1 g) and
- 20 - 0.13 mmol of dithiocarbamate of formula (J)  
(48 mg).

After the tube has been filled, it is  
degassed and vacuum sealed in a manner similar to  
Example 10. The polymerization lasts 64 hours at 80°C.

25 The polymer is recovered by evaporating the  
traces of residual monomer and analysed by GPC in THF  
medium and in polystyrene equivalents. The results are  
as follows:

- degree of conversion: 76%
- number-average molar mass  $M_n = 6700$
- polydispersity index  $PI = 1.2$ .

5

**Example 2.30: vinyl acetate homopolymer**

Introduced into a glass tube are:

- 0.016 mmol of AIBN (2.7 mg),
- 50 mmol of vinyl acetate (4.3 g) and
- 10 - 0.62 mmol of dithiocarbamate of formula (K)  
(251 mg).

After the tube has been filled, it is  
degassed and vacuum sealed in a manner similar to  
Example 2.25. The polymerization lasts 41 hours at  
15 80°C.

The polymer is recovered by evaporating the  
traces of residual monomer and analysed by GPC in THF  
medium and in polystyrene equivalents. The results are  
as follows:

20

- degree of conversion: 47.8%
- number-average molar mass  $M_n = 5000$
- polydispersity index  $PI = 1.43$ .

25

**Example 2.31: ethyl acrylate homopolymer**

Introduced into a glass tube are:

- 0.003 mmol of AIBN (0.56 mg),

- 10 mmol of ethyl acrylate (1 g) and
- 0.12 mmol of dithiocarbamate of formula (K)  
(50 mg).

After the tube has been filled, it is  
 5 degassed and vacuum sealed in a manner similar to  
 Example 2.25. The polymerization lasts 21 hours at  
 80°C.

The polymer is recovered by evaporating the  
 traces of residual monomer and analysed by GPC in THF  
 10 medium and in polystyrene equivalents. The results are  
 as follows:

- degree of conversion: 67%
- number-average molar mass  $M_n = 5900$
- polydispersity index  $PI = 1.22$ .

15

**Example 2.32: styrene homopolymer**

Introduced into a round-bottomed flask are:

- 0.026 mmol of lauroyl peroxide (4.3 mg),
- 20 - 21.3 mmol of styrene (2.22 g) and
- 0.27 mmol of dithiocarbamate of formula (K)  
(108 mg).

The flask is surmounted by a refrigerant,  
 placed under a stream of nitrogen and immersed in an  
 25 oil bath preheated to 115°C. Two new additions of  
 lauroyl peroxide are carried out after two and four  
 hours of reaction (0.026 mmol each time). The reaction  
 is stopped after 24 hours.

The polymer is recovered by evaporating the traces of residual monomer and analysed by GPC in THF medium and in polystyrene equivalents. The results are as follows:

- 5           - degree of conversion: 98%
- number-average molar mass  $M_n = 6700$
- polydispersity index  $PI = 1.7$ .

**Example 2.33: vinyl acetate homopolymer**

10

Introduced into a glass tube are:

- 0.004 mmol of AIBN (0.6 mg),
- 11.6 mmol of vinyl acetate (1 g) and
- 0.146 mmol of dithiocarbamate of formula
- 15 (K) (49.8 mg).

After the tube has been filled, it is degassed and vacuum sealed in a manner similar to Example 2.25. The polymerization lasts 100 hours at 60°C.

20           The polymer is recovered by evaporating the traces of residual monomer and analysed by GPC in THF medium and in polystyrene equivalents. The results are as follows:

- degree of conversion: 71.4%
- 25           - number-average molar mass  $M_n = 5400$
- polydispersity index  $PI = 1.29$ .

### 3 - SYNTHESIS OF BLOCK COPOLYMERS OF FORMULA (IA)

#### Example 3.1: p(EtA-b-St) block copolymer

5 A stock solution is prepared from:

- 4.01 g of ethyl acrylate,
- 0.176 g of dithiocarbamate of formula (A)

and

- 8.8 mg of AIBN.

10 1.06 g of this solution are introduced into a round-bottomed flask. The temperature is raised to 70°C. The polymerization lasts 24 hours after which the traces of residual monomer are removed by evaporation.

A small fraction of the polymer obtained is  
15 removed and analysed by GPC in THF medium and in polystyrene equivalents:

- degree of conversion: 81.5%
- average molecular mass  $M_n = 7300$
- polydispersity index  $PI = 1.4$ .

20 Introduced into the flask are:

- 2.08 g of styrene and
- 4.4 mg of AIBN.

The temperature is raised to 70°C. The  
polymerization lasts 40 hours.

25 The traces of residual monomer are removed by evaporation and the copolymer is analysed by GPC in THF medium and in polystyrene equivalents:

- degree of conversion: 93.8%
- average molecular mass  $M_n = 20,100$
- polydispersity index  $PI = 1.2$ .

5           **Example 3.2: p(EtA-b-VA) block copolymer**

1.38 g of the stock solution prepared for  
Example 3.1 are introduced into a round-bottomed flask.  
The temperature is raised to 70°C. The polymerization  
10 lasts 24 hours after which the traces of residual  
monomer are removed by evaporation.

A small fraction of the polymer obtained is  
removed and analysed by GPC in THF medium and in  
polystyrene equivalents:

- 15
  - degree of conversion: 72.4%
  - average molecular mass  $M_n = 5100$
  - polydispersity index  $PI = 1.4$ .

Introduced into the flask are:

- 20
  - 1.72 g of vinyl acetate and
  - 4.2 mg of AIBN.

The temperature is raised to 70°C. The  
polymerization lasts 40 hours.

The traces of residual monomer are removed by  
evaporation and the copolymer is analysed by GPC in THF  
25 medium and in polystyrene equivalents:

- degree of conversion: 15.6%
- average molecular mass  $M_n = 7200$

- polydispersity index  $PI = 1.5$ .

**Example 3.3: p(St-b-EtA) block copolymer**

5 A stock solution is prepared from:

- 4.01 g of styrene,
- 0.168 g of dithiocarbamate of formula (A)

and

- 8.3 mg of AIBN.

10 1.00 g of this solution is removed and introduced into a round-bottomed flask. The temperature is raised to 70°C. The polymerization lasts 24 hours after which the traces of residual monomer are removed by evaporation.

15 A small fraction of the polymer obtained is removed and analysed by GPC in THF medium and in polystyrene equivalents:

- degree of conversion: 86.9%
- average molecular mass  $M_n = 4500$
- polydispersity index  $PI = 1.3$ .

20 Introduced into the flask are:

- 1.92 g of ethyl acrylate and
- 3.7 mg of AIBN.

The temperature is raised to 70°C. The  
25 polymerization lasts 40 hours.

The traces of residual monomer are removed by evaporation and the copolymer is analysed by GPC in THF medium and in polystyrene equivalents:



- degree of conversion: 94.8%
- average molecular mass  $M_n = 14,100$ .
- polydispersity index  $PI = 1.7$ .

5           **Example 3.4: p(EtA-b-St) block copolymer**

A stock solution is prepared from:

- 7.5 ml of ethyl acrylate
- 3.9 mg of AIBN ( $2.4 \times 10^{-5}$  mol)

10           1.08 ml of this solution are introduced into  
a glass tube and then 50.5 mg ( $1.25 \times 10^{-4}$  mol) of  
precursor of formula K are added. The contents of the  
tube are degassed by three "freeze-vacuum-return to  
ambient" cycles and then vacuum sealed. The tube is  
15 then placed for 21 hours in an oil bath maintained at  
80°C. At the end of the reaction, the tube is opened  
and the monomer residues are removed by vacuum  
evaporation.

              The characteristics of the polymer obtained  
20 are as follows:

- degree of conversion: 67.4%
- average molar mass  $M_n$ : 5500
- polydispersity index  $PI = 1.22$ .

Introduced into a glass tube are:

- 25
- 0.75 g of styrene
  - 1 ml of toluene
  - 1.65 mg of AIBN

- 0.5 g of polyethyl acrylate obtained above.

After the tube has been degassed in the same way as that described above, it is vacuum sealed. After 72 hours at 110°C, the tube is opened and the monomer residues are removed by vacuum evaporation.

The characteristics of the copolymer obtained are as follows:

- degree of conversion: 49.4%
- average molar mass  $M_n$ : 8500
- polydispersity index:  $PI = 1.34$ .

#### **Example 3.5: p(EtA-b-St) block copolymer**

A stock solution is prepared from:

- 5.4 ml of ethyl acrylate
- 3 mg of AIBN ( $2.4 \times 10^{-5}$  mol)

1.08 ml of this solution are introduced into a glass tube and then 41.8 mg ( $1.1 \times 10^{-4}$  mol) of precursor of formula I are added. The contents of the tube are degassed by three "freeze-vacuum-return to ambient" cycles and then vacuum sealed. The tube is then placed for 21 hours in an oil bath maintained at 80°C. At the end of the reaction, the tube is opened and the monomer residues are removed by vacuum evaporation.

The characteristics of the polymer obtained are as follows:

- degree of conversion: 69.7%
- average molar mass  $M_n$ : 7050
- polydispersity index  $PI = 1.2$ .

Introduced into a glass tube are:

5

- 1 g of styrene
- 1 ml of toluene
- 2 mg of AIBN
- 0.72 g of polyethyl acrylate obtained

above.

10

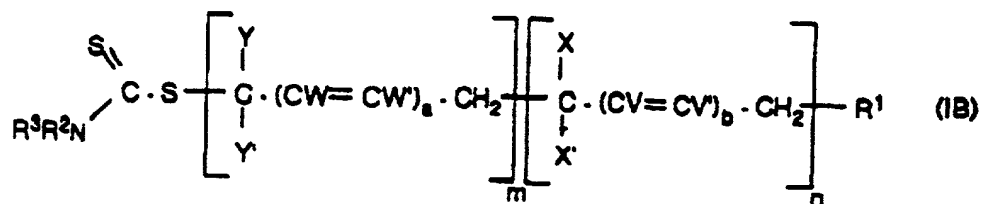
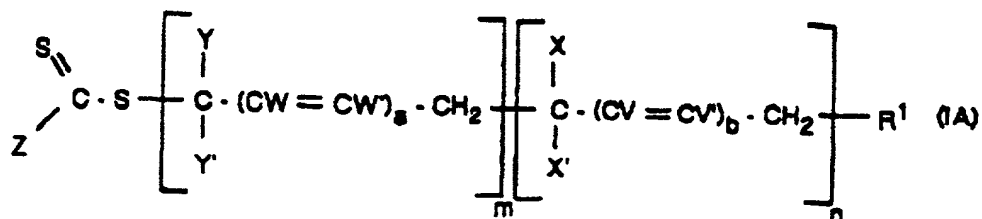
After the tube has been degassed in the same way as that described above, it is vacuum sealed. After 72 hours at 110°C, the tube is opened and the monomer residues are removed by vacuum evaporation.

The characteristics of the copolymer obtained  
15 are as follows:

- degree of conversion: 26.1%
- average molar mass  $M_n$ : 12,900
- polydispersity index:  $PI = 1.29$ .

## CLAIMS

1. Process for preparing block polymers of general formula (IA) or (IB):



5

in which formulae:

-  $\text{R}^1$  represents:

- an optionally substituted alkyl, acyl, aryl, alkene or alkyne group (i), or
- 10 • an optionally substituted or aromatic, saturated or unsaturated, carbocycle (ii), or
- an optionally substituted or aromatic, saturated or unsaturated, heterocycle (iii),

it being possible for these groups and rings (i),

15 (ii) and (iii) to be substituted with substituted

phenyl groups, substituted aromatic groups, or

groups: alkoxycarbonyl or aryloxycarbonyl ( $-\text{COOR}$ ),

carboxyl ( $-\text{COOH}$ ), acyloxy ( $-\text{O}_2\text{CR}$ ), carbamoyl ( $-\text{CONR}_2$ ),

cyano ( $-\text{CN}$ ), alkylcarbonyl, alkylarylcarbonyl,

arylcarbonyl, arylalkylcarbonyl, phthalimido, maleimido, succinimido, amidino, guanidimo, hydroxyl (-OH), amino (-NR<sub>2</sub>), halogen, allyl, epoxy, alkoxy (-OR), S-alkyl, S-aryl, organosilyl, groups having a hydrophilic or ionic character, such as the alkali metal salts of carboxylic acids, the alkali metal salts of sulphonic acid, polyalkylene oxide chains (PEO, PPO), cationic substituents (quaternary ammonium salts),

10 R representing an alkyl or aryl group,

- Z is an optionally substituted ring comprising a nitrogen atom via which Z is linked to the C(=S)-S-group of formula (IA), the other atoms of the said ring inducing a delocalizing or electron-withdrawing effect with respect to the electron density of the nitrogen atom,

-R<sup>2</sup> and R<sup>3</sup>, which are identical or different, represent:

- an optionally substituted alkyl, acyl, aryl, alkene or alkyne group (i), or
- 20 • an optionally substituted or aromatic, saturated or unsaturated, carbocycle (ii), or
- an optionally substituted, saturated or unsaturated, heterocycle (iii),

it being possible for these groups and rings (i),

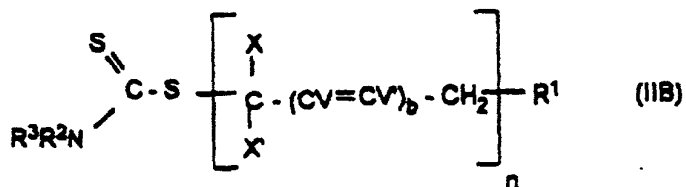
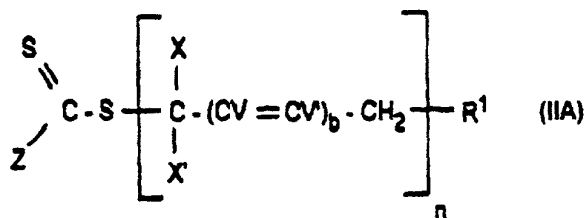
25 (ii) and (iii) to be substituted with:

- . substituted phenyl groups or substituted aromatic groups,
- . groups: alkoxycarbonyl or aryloxycarbonyl

- (-COOR), carboxyl (-COOH), acyloxy (-O<sub>2</sub>CR),  
 carbamoyl (-CONR<sub>2</sub>), cyano (-CN), alkylcarbonyl,  
 alkylarylcarbonyl, arylcarbonyl,  
 arylalkylcarbonyl, phthalimido, maleimido,  
 5 succinimido, amidino, guanidimo, hydroxyl (-OH),  
 amino (-NR<sub>2</sub>), halogen, allyl, epoxy, alkoxy (-OR),  
 S-alkyl, S-aryl,  
 . groups having a hydrophilic or ionic character,  
 such as the alkali metal salts of carboxylic  
 10 acids, the alkali metal salts of sulphonic acid,  
 polyalkylene oxide chains (PEO, PPO), cationic  
 substituents (quaternary ammonium salts),  
 R representing an alkyl or aryl group,  
 and, for at least R<sup>2</sup> or R<sup>3</sup>, these groups and rings (i),  
 15 (ii) and (iii) induce a delocalizing or electron-  
 withdrawing effect with respect to the electron density  
 of the nitrogen atom to which R<sup>2</sup> and R<sup>3</sup> are linked,  
 - V, V', W and W', which are identical or different,  
 represent: H, an alkyl group or a halogen,  
 20 - X, X', Y and Y', which are identical or different,  
 represent H, a halogen or a group chosen from R', OR',  
 OCOR', NHCOH, OH, NH<sub>2</sub>, NHR', N(R')<sub>2</sub>, (R')<sub>2</sub>N'O<sup>-</sup>, NHCOR',  
 CO<sub>2</sub>H, CO<sub>2</sub>R', CN, CONH<sub>2</sub>, CONHR' or CONR'<sub>2</sub>, in which R' is  
 25 chosen from alkyl, aryl, aralkyl, alkaryl, alkene or  
 organosilyl groups, optionally perfluorinated and  
 optionally substituted with one or more carboxyl,  
 epoxy, hydroxyl, alkoxy, amino, halogen or sulphonic  
 groups,

- **a** and **b**, which are identical or different, are equal to 0 or 1,
  - **m** and **n**, which are identical or different, are greater than or equal to 1 and, when one or other is greater than 1, the individual repeat units are identical or different,
- in which process the following are brought into contact with each other:

- an ethylenically unsaturated monomer of formula:
- 10  $CYY' (=CW-CW')_a=CH_2$ ,
- a precursor compound of general formula (IIA) or (IIB):



- 15 in which Z, X, X', V, V', R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> have the same meaning, and b and n the same value, as previously;
- a radical polymerization initiator.

2. Process according to claim 1, characterized in that the ethylenically unsaturated monomer is chosen

20 from: styrene or its derivatives, butadiene,

chloroprene, (meth)acrylic esters and vinyl nitriles.

3. Process according to claim 1 or 2,  
characterized in that, in compounds of formula (IA) and  
(IIA), the ring Z is a ring based on carbon atoms.

5           4.    Process according to any one of the preceding  
claims, characterized in that the ring Z includes at  
least one heteroatom other than the nitrogen which  
links the ring Z to  $-C(=S)S$ , this heteroatom being  
chosen from O, S, N and/or P.

10           5.     Process according to any one of the preceding  
claims, characterized in that, in the compounds of  
formula (IA) and (IIA), the ring Z is an aromatic ring.

6. Process according to any one of the preceding claims, characterized in that, in the compounds of formula (IA) and (IIA), the ring Z comprises at least one of the following functional groups: carbonyl ( $C=O$ ),  $SO_2$ ,  $POR''$ ,  $R''$  representing an alkyl, aryl, OR, SR or  $NR_2$  group, where the R is identical or different and represents an alkyl or aryl group.

20           7.     Process according to any one of the preceding  
claims, characterized in that, in the compounds of  
formula (IA) and (IIA), the ring Z is substituted with  
at least one of the following groups: alkyl, aryl,  
alkoxycarbonyl or aryloxycarbonyl (-COOR), carboxyl  
25 (-COOH), acyloxy (-O<sub>2</sub>CR), carbamoyl (-CONR<sub>2</sub>), cyano  
(-CN), alkylcarbonyl, alkylarylcarbonyl, arylcarbonyl,  
arylalkylcarbonyl, phthalimido, maleimido, succinimido,  
amidino, guanidimo, hydroxyl (-OH), amino (-NR<sub>2</sub>),



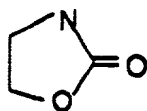
halogen, allyl, epoxy, alkoxy (-OR), S-alkyl, S-aryl, groups having a hydrophilic or ionic character, such as the alkali metal salts of carboxylic acids or the alkali metal salts of sulphonic acid, polyalkylene  
 5 oxide chains (PEO, PPO), cationic substituents (quaternary ammonium salts), R representing an alkyl or aryl group.

8. Process according to any one of the preceding claims, characterized in that, in the compounds of  
 10 formula (IA) and (IIA), the ring Z is substituted with at least one carbocycle or a heterocycle, this being optionally aromatic and/or substituted.

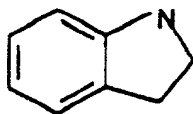
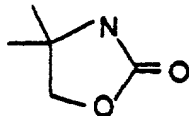
9. Process according to the preceding claim, characterized in that, in the compounds of formula (IA)  
 15 and (IIA), the ring Z and its cyclic substituent have two common atoms.

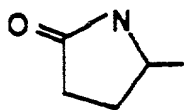
10. Process according to any one of the preceding claims, characterized in that the ring Z is chosen from one of the following rings:

20

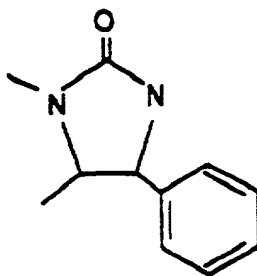


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10 11. Process according to claim 1, characterized in that, in the case of the compounds of formula (IB) and (IIB),  $R^2$  and/or  $R^3$  exert a  $\pi$  withdrawing effect.

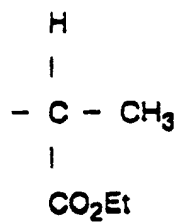
12. Process according to claim 11, characterized in that  $R^2$  and/or  $R^3$  represent a carbonyl or  
15 (hetero)aromatic group.

13. Process according to claim 1, characterized in that, in the case of the compounds of formula (IB) and (IIB),  $R^2$  and/or  $R^3$  exert a  $\Sigma$  withdrawing effect.

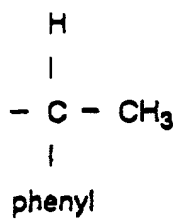
14. Process according to claim 1 or 13,  
20 characterized in that  $R^2$  and/or  $R^3$  represent an alkyl group substituted with electron-withdrawing groups.

15. Process according to any one of the preceding claims, characterized in that  $R^1$  is chosen from the groups:

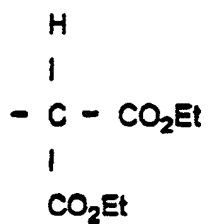
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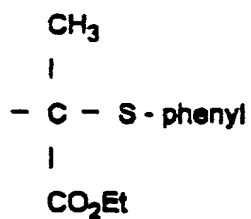
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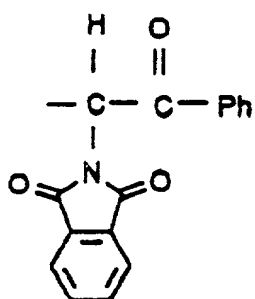
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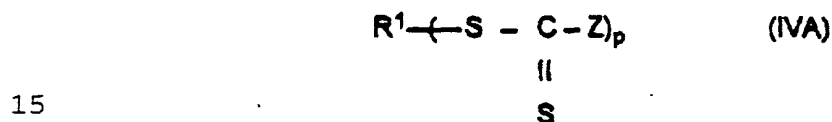
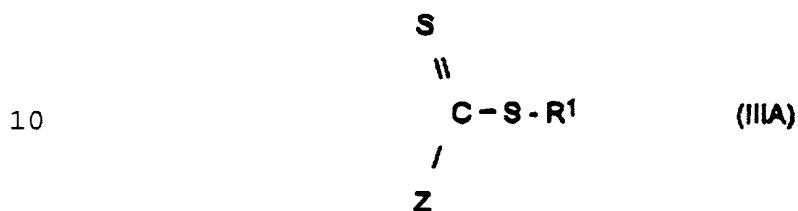


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16. Process according to any one of claims 1 to 10 and 15 to 6, characterized in that the precursor

compound of general formula (IIA) is a polymer and in that the said polymer comes from the radical polymerization of an ethylenically unsaturated monomer of formula:  $CXX' (=CV-CV')_p=CH_2$  during which the said

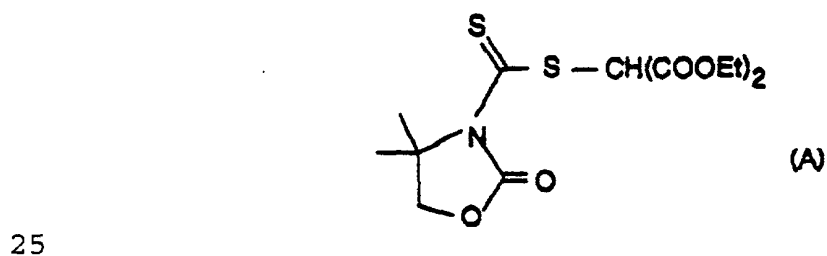
5 monomer is brought into contact with a radical polymerization initiator and a compound of general formula (IIIA) or (IVA):



p being between 2 and 10.

17. Process according to the preceding claim, characterized in that the compound of formula (IIIA) is

20 chosen from compounds of the following formulae:



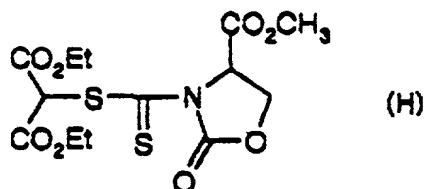
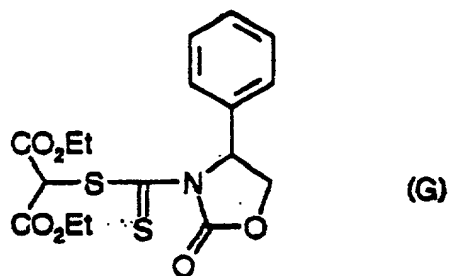
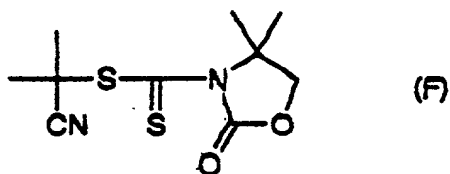
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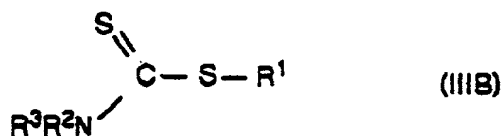


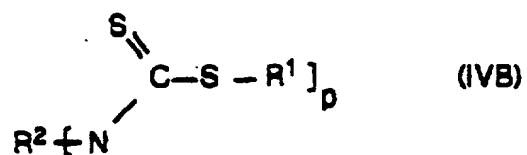
18. Process according to any one of claims 1 and 11 to 16, characterized in that the precursor compound of general formula (IIB) is a polymer and in that the said polymer comes from the radical polymerization of an ethylenically unsaturated monomer of formula:

$$\text{CXX}'(=\text{CV}-\text{CV}')_n=\text{CH}_2$$

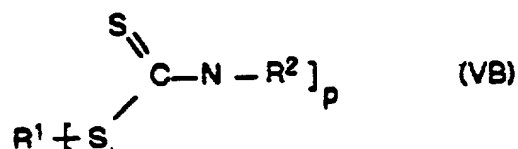
during which the said monomer is brought into contact with a radical polymerization initiator and a compound of general formula (IIIB),

(IVB) or (VB):





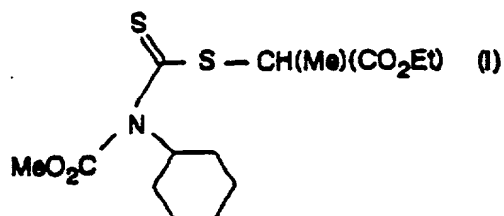
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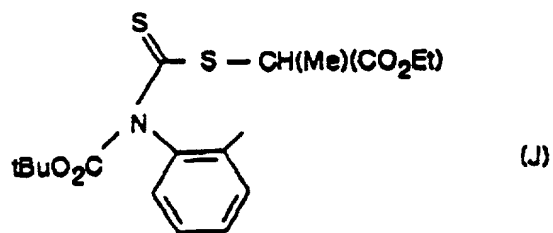
$p$  being between 2 and 10.

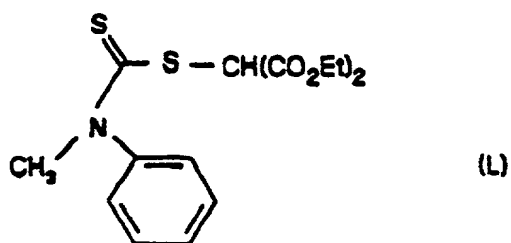
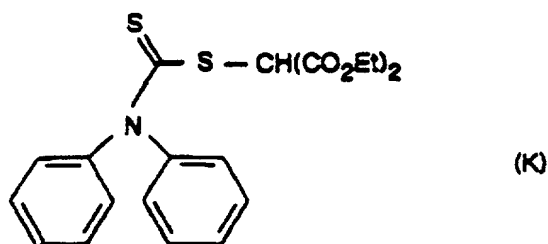
- 10      19. Process according to the preceding claim,  
characterized in that the compound of formula (IIIB) is  
chosen from the compounds of the following formulae:

15



20





20. Process for preparing multiblock polymers, characterized in that the implementation of the process according to one of claims 1 to 15 is repeated at least 15 once, using:

- different monomers from those of the previous implementation, and
- instead of the precursor compound of formula (IIA) or (IIB), the block polymer coming from the previous 20 implementation.

21. Block polymer capable of being obtained by the process according to one of the preceding claims.

22. Block polymer according to the preceding claim, characterized in that it has a polydispersity 25 index of at most 2.

23. Block polymer according to the preceding claim, characterized in that it has a polydispersity index of at most 1.5.



24. Block polymer according to any one of claims 21 to 23, characterized in that it has at least two polymer blocks chosen from the following combinations:

- polystyrene/polymethyl acrylate,
- 5 - polystyrene/polyethyl acrylate,
- polystyrene/poly(*tert*-butyl acrylate),
- polyethyl acrylate/polyvinyl acetate,
- polybutyl acrylate/polyvinyl acetate,
- poly(*tert*-butyl acrylate)/polyvinyl acetate.

10 25. Polymer capable of being obtained by the process which consists in bringing an ethylenically unsaturated monomer of formula:  $CXX' (=CV-CV')_b=CH_2$ , a radical polymerization initiator and a compound of formula (IIIA), (IIIB), (IVA), (IVB) or (VB) into  
15 contact with one another.

26. Polymer according to claim 25, characterized in that it has a polydispersity index of at most 2.

27. Polymer according to claim 25 or 26, characterized in that it has a polydispersity index of  
20 at most 1.5.

28. Compound of general formula (IIA) or (IIB), characterized in that it has a polydispersity index of at most 2.

**PROCESS FOR SYNTHESIZING BLOCK POLYMERS  
BY CONTROLLED RADICAL POLYMERIZATION  
FROM DITHIOCARBAMATE COMPOUNDS**

Abstract of the Disclosure

The invention concerns a polymerisation method for block polymers which consists in contacting: an ethylenically unsaturated monomer of formula:  $CYY'$   $(=CW-CW')_a = CH_2$ , a precursor compound of general formula (IIA) or (IIB), and a radical polymerisation initiator.

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COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY (include Reference to PCT International Applications) PCT/FR98/02867	ATTORNEY'S DOCKET NO <b>RN97162G1</b>
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As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

**PROCESS FOR SYNTHESIZING BLOCK POLYMERS BY CONTROLLED RADICAL POLYMERIZATION FROM DITHIOCARBAMATE COMPOUNDS**

the specification of which (check only one item below):

☐ is attached hereto.

☐ was filed as United States application

Serial No. \_\_\_\_\_

on \_\_\_\_\_

and was amended

on \_\_\_\_\_ (if applicable)

☒ was filed as PCT international application

Number **PCT/ FR98/02867** \_\_\_\_\_

on **Filed December 23, 1998** \_\_\_\_\_

and amended under PCT ARTICLE 19

on \_\_\_\_\_ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations. §1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:

PRIOR FOREIGN/PCT APPLICATION(S) AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. 119:				
COUNTRY PCT indicate PCT	APPLICATION NUMBER	DATE OF FILING (day month year)	PRIORITY CLAIMED UNDER 35 USC 119	
FRANCE	97 16779	31 December 1997	<input checked="" type="checkbox"/> YES	<input type="checkbox"/> NO
FRANCE	98 09780	30 July 1998	<input checked="" type="checkbox"/> YES	<input type="checkbox"/> NO
			<input type="checkbox"/> YES	<input type="checkbox"/> NO
			<input type="checkbox"/> YES	<input type="checkbox"/> NO
			<input type="checkbox"/> YES	<input type="checkbox"/> NO

<b>COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY</b> (Continued) (include Reference to PCT International Applications) <b>PCT/FR98/02867</b>				ATTORNEY'S DOCKET NO <b>RN97162G1</b>	
I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application(s) and the national or PCT international filing date of this application:					
PRIOR U.S. APPLICATIONS OR PCT INTERNATIONAL APPLICATIONS DESIGNATING THE U.S. FOR BENEFIT UNDER 35 U.S.C. 120					
U.S. APPLICATIONS			STATUS (CHECK ONE)		
U.S. APPLICATION NUMBER	U.S. FILING DATE	PATENTED	PENDING	ABANDONED	
PCT APPLICATIONS DESIGNATING THE U.S.					
PCT APPLICATION NO	PCT FILING DATE	US SERIAL NUMBERS ASSIGNED (if any)			
<b>POWER OF ATTORNEY:</b> As a named inventor, I hereby appoint the following attorney's and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith (List name and registration number) <b>JOHN A. SHEDDEN - Reg. No. 25,644,</b> <b>JOHN D. WOOD - Reg. No. 31,146</b> <span style="float: right; border: 1px solid black; border-radius: 50%; padding: 2px 10px;">2</span> <b>JEAN-LOUIS SEUGNET - Limited Recognition under 37 CFR § 10.9(b) enclosed.</b>					
Send Correspondence to: <b>Jean-Louis SEUGNET</b> Intellectual Property Dept. RHODIA INC. 259 PROSPECT PLAINS ROAD, CN 7500 CRANBURY, NJ 08512-7500			Direct Telephone Calls to: <small>(name and telephone number)</small> <b>Jean-Louis SEUGNET</b> (609) 860-4180		
201	FULL NAME OF INVENTOR	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME	
	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP	
	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY	
202	FULL NAME OF INVENTOR	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME	
	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP	
	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY	
203	FULL NAME OF INVENTOR	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME	
	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP	
	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY	
I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.					
SIGNATURE OF INVENTOR 201		SIGNATURE OF INVENTOR 202		SIGNATURE OF INVENTOR 203	
DATE		DATE		DATE	

<b>COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY</b> (Continued) (include Reference to PCT International Applications) <b>PCT/FR98/02867</b>					ATTORNEY'S DOCKET NO <b>RN97162G1</b>	
I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application(s) and the national or PCT international filing date of this application:						
PRIOR U.S. APPLICATIONS OR PCT INTERNATIONAL APPLICATIONS DESIGNATING THE U.S. FOR BENEFIT UNDER 35 U.S.C. 120						
U.S. APPLICATIONS			STATUS (CHECK ONE)			
U.S. APPLICATION NUMBER	U.S. FILING DATE	PATENTED	PENDING	ABANDONED		
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Send Correspondence to: <b>Jean-Louis SEUGNET</b> Intellectual Property Dept. <b>RHODIA INC.</b> <b>259 PROSPECT PLAINS ROAD,</b> <b>CN 7500</b> <b>CRANBURY, NJ 08512-7500</b>				Direct Telephone Calls to: <small>(name and telephone number)</small> <b>Jean-Louis SEUGNET</b> <b>(609) 860-4180</b>		
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	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY		
I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.						
SIGNATURE OF INVENTOR 201		SIGNATURE OF INVENTOR 202		SIGNATURE OF INVENTOR 203		
DATE		DATE		DATE		

<b>COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY</b> (Continued) (include Reference to PCT International Applications) <b>PCT/FR98/02867</b>				ATTORNEY'S DOCKET NO <b>RN97162G1</b>	
I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application(s) and the national or PCT international filing date of this application:					
PRIOR U.S. APPLICATIONS OR PCT INTERNATIONAL APPLICATIONS DESIGNATING THE U.S. FOR BENEFIT UNDER 35 U.S.C. 120					
U.S. APPLICATIONS			STATUS (CHECK ONE)		
U.S. APPLICATION NUMBER	U.S. FILING DATE	PATENTED	PENDING	ABANDONED	
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	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY	
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	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY	
203	FULL NAME OF INVENTOR	FAMILY NAME	FIRST GIVEN	SECOND GIVEN NAME	
	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP	
	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY	
I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.					
SIGNATURE OF INVENTOR 201		SIGNATURE OF INVENTOR 202		SIGNATURE OF INVENTOR 203	
DATE		DATE		DATE	

<b>COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY</b> (Continued) (include Reference to PCT International Applications) <b>PCT/FR98/02867</b>				ATTORNEY'S DOCKET NO <b>RN97162G1</b>	
I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application(s) and the national or PCT international filing date of this application:					
PRIOR U.S. APPLICATIONS OR PCT INTERNATIONAL APPLICATIONS DESIGNATING THE U.S. FOR BENEFIT UNDER 35 U.S.C. 120					
U.S. APPLICATIONS			STATUS (CHECK ONE)		
U.S. APPLICATION NUMBER	U.S. FILING DATE	PATENTED	PENDING	ABANDONED	
PCT APPLICATIONS DESIGNATING THE U.S.					
PCT APPLICATION NO	PCT FILING DATE	US SERIAL NUMBERS ASSIGNED (if any)			
<b>POWER OF ATTORNEY:</b> As a named inventor, I hereby appoint the following attorney's and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith (List name and registration number) <b>JOHN A. SHEDDEN - Reg. No. 25,644,</b> <b>JOHN D. WOOD - Reg. No. 31,146</b> <b>JEAN-LOUIS SEUGNET - Limited Recognition under 37 CFR § 10.9(b) enclosed</b>					
Send Correspondence to: <b>JEAN-LOUIS SEUGNET</b> <b>INTELLECTUAL PROPERTY DEPT.</b> <b>RHODIA INC.</b> <b>259 PROSPECT PLAINS ROAD,</b> <b>CN 7500, CRANBURY, NJ 08512-7500</b>			Direct Telephone Calls to: <small>(name and telephone number)</small> <b>JEAN-LOUIS SEUGNET</b> <b>(609) 860-4180</b>		
204	FULL NAME OF INVENTOR	FAMILY NAME	FIRST GIVEN	SECOND GIVEN NAME	
		<b>FRANCK</b>	<b>Xavier</b>		
	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP	
		<b>CHEVILLY LARUE</b>	<b>FRANCE</b>	<b>FRANCE</b>	
	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY	
		<b>6, rue Paul Hochart</b>	<b>CHEVILLY LARUE</b>	<b>F-94550, FRANCE</b>	
205	FULL NAME OF INVENTOR	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME	
		<b>BOUHADIR</b>	<b>Ghenwa</b>		
	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP	
		<b>Gif sur Yvette</b>	<b>FRANCE</b>	<b>LEBANON</b>	
	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY	
		<b>11, residence du Chateau de Courcelles</b>	<b>Gif sur Yvette</b>	<b>F-91190, FRANCE</b>	
206	FULL NAME OF INVENTOR	FAMILY NAME	FIRST GIVEN	SECOND GIVEN NAME	
	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP	
	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY	
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SIGNATURE OF INVENTOR 204		SIGNATURE OF INVENTOR 205		SIGNATURE OF INVENTOR 206	
DATE		DATE		DATE	

<b>COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY</b> (Continued) (include Reference to PCT International Applications) <b>PCT/FR98/02867</b>				ATTORNEY'S DOCKET NO <b>RN97162G1</b>	
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PRIOR U.S. APPLICATIONS OR PCT INTERNATIONAL APPLICATIONS DESIGNATING THE U.S. FOR BENEFIT UNDER 35 U.S.C. 120					
U.S. APPLICATIONS			STATUS (CHECK ONE)		
U.S. APPLICATION NUMBER	U.S. FILING DATE	PATENTED	PENDING	ABANDONED	
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204	FULL NAME OF INVENTOR	FAMILY NAME <b>FRANCK</b>	FIRST GIVEN <b>Xavier</b>	SECOND GIVEN NAME	
	RESIDENCE & CITIZENSHIP	CITY <b>CHEVILLY LARUE</b>	STATE OR FOREIGN COUNTRY <b>FRANCE</b>	COUNTRY OF CITIZENSHIP <b>FRANCE</b>	
	POST OFFICE ADDRESS	POST OFFICE ADDRESS <b>6, rue Paul Hochart</b>	CITY <b>CHEVILLY LARUE</b>	STATE & ZIP CODE/COUNTRY <b>F-94550, FRANCE</b>	
205	FULL NAME OF INVENTOR	FAMILY NAME <b>BOUHADIR</b>	FIRST GIVEN NAME <b>Ghenwa</b>	SECOND GIVEN NAME	
	RESIDENCE & CITIZENSHIP	CITY <b>Gif sur Yvette</b>	STATE OR FOREIGN COUNTRY <b>FRANCE</b>	COUNTRY OF CITIZENSHIP <b>LEBANON</b>	
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SIGNATURE OF INVENTOR 204		SIGNATURE OF INVENTOR 205 <i>[Signature]</i>		SIGNATURE OF INVENTOR 206	
DATE		DATE <b>03/07/2000</b>		DATE	